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THERMODYNAMIC PROPERTIES OF NON-MAGNETIC METALLIC SYSTEMS DUE TO THE ELECTRON-ION INTERACTION

by

© WILLIAM P. O'LEARY,

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled THERMODYNAMIC PROPERTIES OF NON-MAGNETIC METALLIC SYSTEMS DUE TO THE ELECTRON-ION INTERACTION submitted by William P. O'Leary in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Theoretical Physics.

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ABSTRACT

A formalism is developed to describe those thermodynamic properties of a metallic system which are due to the electron-ion interaction. It is shown, in second order perturbation theory, that the free energy due to this interaction may be expressed as a simple formula involving the electron-ion pseudopotentials and the dynamical structure factors of the ionic system.

The result may be applied to the usual range of substances which lend themselves to pseudopotential treatment, and possesses considerable generality. It may be applied to pure metals and alloys (whether solid or liquid), allowing for full generality of the ion dynamics, and including those alloys in which mass differences and lattice distortion effects are important.

A number of well known but diverse results are obtained as special cases of the general formalism, and some numerical calculations are performed as illustrative examples.

A particular example is the case of Ag-Au alloys. The deviation from linearity (in concentration) of the low-temperature specific heat coefficient has been the object of some interest in recent years, and a mechanism, the dynamic "interference" part of the electron-ion

interaction, is proposed, which seems to adequately account for the observed behaviour, both in general magnitude and concentration dependence.

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INTRODUCTION

§0.1 General Remarks

In the past 30 years or so, theoretical understanding of the properties of metals and alloys has progressed considerably; and one of the areas in this field receiving particular attention has been the attempt to enumerate and explain those phenomena or properties which arise specifically from the interaction between the conduction electrons and the constituent ions of such substances.

The present work will be primarily concerned with the development of a formalism which can be used to investigate those thermodynamic properties of metallic systems which arise from the electron-ion interaction.

The formalism will apply to pure metals and alloys and will, in its most general cases, be applicable to those substances in which mass, size, and force constant differences play a significant role.

It has been known for a long time that, in investigating the electronic properties of metals, considerable qualitative success can be obtained by treating a metal as a collection of stationary ions interacting, through a weak potential, with a "gas" of conduction electrons [1].

The success of this "Nearly Free Electron" model would, at first sight, seem to be rather anomalous. The electron-ion interaction is essentially a Coulomb potential; and for an electron close to the nucleus of an ion, the attractive force is very large.

The first major contribution to our understanding of this problem came in 1928 when Bloch [2] showed that an electron moving in a perfectly periodic potential is not subject to any scattering, apart from elastic Bragg reflections. Thus, in the case of a pure crystalline solid, one may argue that if all the ions were stationary, and fixed at sites on a perfect lattice, then the valence electrons would travel unhampered through the resulting periodic structure.

It would then be the deviations from periodicity due to ionic vibrations, vacancies, impurities etc., that cause the electrons to be affected by the ions, and to have their dynamical properties altered from those of a free "gas". In this way, any scattering of electrons by the ions would be due to the <u>difference</u> between the <u>actual</u> ionic potential and the <u>periodic</u> potential of a pure static solid. Under many circumstances one could reasonably expect this net interaction to be small.

If one turns to amorphous or liquid metals, however, the situation should be quite different, if one were to use the same line of reasoning. Here one does not have the initial periodic structure from which to calculate deviations in the ionic potential, and there is no reason to suppose that the electron-ion interaction would not be quite large indeed.

Experimentally one knows, of course, that while there are marked changes, the electronic properties of a liquid metal are not enormously different from those of the corresponding solid. The resistivity of most metals, for example, increases upon melting; but in most cases $\rho_{liquid} \sim 2\rho_{solid}$ or less, at the melting point [1]. This indicates that the scattering of electrons does not increase in any drastic fashion in a non-periodic structure, and that even in liquid metals the electron-ion interaction is rather weak, in most cases.

§0.2 Pseudopotentials

The resolution of these difficulties arose ultimately out of the "Orthogonalized Plane Wave" (OPW) approach to energy band calculations developed by Herring in 1940 [3,4]. By 1959, Phillips and Kleinman [5] and Antončik [6] had recast this procedure into what is now called "Pseudopotential Theory"; and the

subsequent activity along these lines has led to a greatly improved understanding of what goes on in metallic substances. See [7] for a recent review.

This method starts by dividing the electrons in a metal into two types, namely, "core" electrons and "valence" or "conduction" electrons. The former are bound to, and localized around, individual nuclei, while the latter are not bound to particular ions, and are thus able to move through the body of the metal.

For the limiting case of no electron-ion interaction, the wave function of a conduction electron would be a plane wave. Thus one expresses the wave function of a conduction electron as a sum of OPW's, which look like plane waves in regions away from the nuclei, but are constructed so as to be orthogonal to all the core states. This orthogonality condition must be observed, since the conduction electrons simply occupy higher states (in energy) of the same Hamiltonian governing the behaviour of the core electrons.

Having set up the problem in this way, it is then possible to rework the Schrödinger equation for the conduction electrons into a form which is reduced to finding the rapidly converging plane wave solution to a Schrödinger equation with a modified potential. This "pseudopotential", then, consists of the original one,

plus a non-local part involving the wave functions of the core electrons.

The net result is that the strong part of the original interaction (which is near the nucleus) is removed, and we are left with the effective interaction between the ions and the conduction electrons. Now this potential will be weak, in the sense that it will not have any bound states, but will not always be weak in an absolute sense. This need not be an obstacle in practical calculations, however, since the NFE model will be applicable to a given substance if the net scattering of a conduction electron from an ion is small. The principal restrictions are that multiple scattering effects must be negligible, and that the wave-functions of core electrons on adjacent ions do not appreciably overlap.

One important aspect of these developments is that one can visualize, especially in those cases where non-local effects are minimal, a metallic substance as a collection of "pseudo-atoms" which individually cause weak scattering of conduction electrons. This concept is not restricted to periodic structures, or those which are nearly so, and one is thus able to treat liquids and disordered substances on much the same basis as regular solids. In the light of this then, the "nearly

free" behaviour of metallic electrons is seen to be a reasonable state of affairs.

§0.3 Aim of Present Work

The present work is intended to apply to those metals and alloys where the pseudopotentials are such that the scattering of conduction electrons may be treated adequately in the Born approximation.

In the same spirit, a perturbative approach is used to calculate the contribution to the free energy due to the interaction between the electrons and ions which constitute the metallic substance under consideration. It is well known [8] that perturbation theory applied to the free energy has the advantage that the contributions in each order do not involve the singularities which may arise when perturbation theory is applied to the Hamiltonian; and as such, is more appropriate for systems having degenerate states.

It is found that, to second order in the perturbation, the free energy of a metallic system, arising from the electron-ion pseudopotential interaction, may be expressed simply in terms of a scattering function $\Gamma(\underset{\sim}{Q},\omega)$, which, for a pure substance, is closely related to the Van Hove [9] dynamical structure factor $S(\underset{\sim}{Q},\omega)$.

Knowing the free energy ϕ, one may then calculate any of the other thermodynamic properties which are related to it by standard expression. For the internal energy and specific heat we have, for example:

$$\bar{E} = \phi - T\left(\frac{\partial \phi}{\partial T}\right) \quad ; \qquad C_V = -T\left(\frac{\partial^2 \phi}{\partial T^2}\right) \quad .$$

§0.4 Previous Work

The specific heat of metallic systems is the subject of much interest, and will be treated in applications in a later chapter. It would then seem appropriate, at this point, to review some of the previous work done in this area, using various techniques, in order to help put the results of the present work into proper perspective.

In 1954 Buckingham and Schafroth [10] did a free energy perturbation calculation, using a simplified electron-phonon interaction to approximate the electron-ion interaction in a pure metal. Their object was to determine how the electronic specific heat differed from the free-electron value because of the interaction.

They demonstrated that the electronic specific heat coefficient was increased appreciably at $T = 0°K$, increased somewhat more as temperature was raised, and then decreased, so that at high enough temperatures it yielded the free electron value.

In the years following this work, a number of workers have undertaken investigations with a view to obtaining a more complete and accurate understanding of this problem.

These efforts have been directed at various aspects of the problem, such as: obtaining results that are valid when the interaction is not small, largely through the use of Green's function techniques; using more realistic electron-ion interactions, usually including the effects of Umklapp processes; and considering the effect of the direct interaction between the electrons.

The works of Migdal [11], Nakajima and Watabe [12], Ashcroft and Wilkins [13], and Rice [14] will serve to illustrate these developments; and the situation as of about 1968 is reviewed at some length by Wilkins in his lecture volume "Observable Many-Body Effects in Metals" [15].

At low temperatures, Wilkins shows that the initial increase of the electron-phonon enhancement is principally due to a T^2 ℓn T term, as was originally indicated by Buckingham and Schafroth.

At high temperatures, his calculations imply that the change in the specific heat actually becomes negative; and thus the free-electron value is approached from below roughly as $1/T^2$.

In the case of metal alloys, of course, the situation is more complex, and the scattering of conduction electrons is altered by a number of important factors. The variation of the ionic potential from site to site, and the localized constrictions or dilations of the lattice, due to differences in atomic volume, have a direct effect on the scattering of conduction electrons. In addition to this, the potential, volume, and mass differences between the individual species alter the dynamic properties of the lattice, and this in turn causes further changes in electron scattering.

Two aspects of the alloy specific heat problem have received particular attention in recent years, namely, the changes due to the potential differences, and those due to the altered emission and absorption of lattice vibrational quanta. Papers by Stern and by Haga [17], as well as the references cited in these works will give a good indication of the type of effort that has been made to date. The present work will look at these effects in a unified way, as a special application of the general results, in Chapter 4.

§0.5 Plan of the Thesis

The thesis is divided into four principal chapters, with a short fifth chapter to summarize the results and

conclusions of the work.

In Chapter 1 we will develop the main result of the thesis, and comment on its applicability. Chapter 2 will be concerned with the dynamical structure factors which, along with the electron-ion pseudopotentials, are of central importance to the formalism of Chapter 1.

In Chapter 3 we will show how one may obtain some well known, but diverse results, as special cases of the formalism, and will derive a concise expression for the low-temperature electronic specific heat changes in an alloy, due to the dynamic part of the electron-ion interaction.

Chapter 4 contains the results of some simple numerical calculations. The electron-phonon enhancement for Na is calculated, and the behaviour of the "interference" and "impurity" contributions to the specific heat is investigated for a series of "theoretical" alloys whose pseudopotentials are similar to that of Na.

In addition to this, we calculate the electron phonon enhancement for Ag and Au, and propose an explanation for the concentration dependence of the electronic specific heat coefficient in Ag-Au alloys, in terms of the dynamic "interference" part of the electron-ion interaction.

CHAPTER 1

FORMALISM

§1.1 Operator Expansion

In this Section we describe the operator expansion that will be needed in the subsequent development.

Consider an operator Λ, and an arbitrary function of this operator which can be expressed as a power series: $F(\Lambda) = \sum_{n=0}^{\infty} C_n \Lambda^n$. Then take Λ to be further given by $\Lambda = \Lambda_o + \varepsilon\Lambda_1$, where Λ_o is an operator whose eigen-problem is assumed to be already solved: $\Lambda_o|\alpha\rangle = \lambda_\alpha|\alpha\rangle$, and ε is the usual expansion parameter used here to keep track of terms, and will be put equal to unity at the end. We will want matrix elements of $F(\Lambda)$ between eigenstate of Λ_o. This expansion was treated by Schafroth in 1951 [18], and the result is as follows:

$$\langle\alpha|F(\Lambda)|\alpha'\rangle = \langle\alpha|\alpha'\rangle F(\lambda_\alpha) + \varepsilon\langle\alpha|\Lambda_1|\alpha'\rangle\{\frac{F(\lambda_\alpha)}{\lambda_\alpha-\lambda_{\alpha'}} + \frac{F(\lambda_{\alpha'})}{\lambda_{\alpha'}-\lambda_\alpha}\}$$

$$+ \varepsilon^2 \sum_{\alpha''}\langle\alpha|\Lambda_1|\alpha''\rangle\langle\alpha''|\Lambda_1|\alpha'\rangle\{\frac{F(\lambda_\alpha)}{(\lambda_\alpha-\lambda_{\alpha'})(\lambda_\alpha-\lambda_{\alpha''})}$$

$$+ \frac{F(\lambda_{\alpha'})}{(\lambda_{\alpha'}-\lambda_\alpha)(\lambda_{\alpha'}-\lambda_{\alpha''})} + \frac{F(\lambda_{\alpha''})}{(\lambda_{\alpha''}-\lambda_\alpha)(\lambda_{\alpha''}-\lambda_{\alpha'})}\} + O(\varepsilon^3) \ .$$

Note that for $\alpha' \to \alpha$, the first $\{\ldots\} \to F'(\lambda_\alpha)$, and for $\alpha'' \to \alpha' \to \alpha$, the second $\{\ldots\} \to \frac{1}{2!} F''(\lambda_\alpha)$, etc., so that

if the $|\alpha>$'s are also eigenstates of Λ_1, we obtain the ordinary Taylor expansion. The diagonal terms are seen to be:

$$<\alpha|F(\Lambda)|\alpha> = F(\lambda_\alpha) + \varepsilon<\alpha|\Lambda_1|\alpha>F'(\lambda_\alpha)$$

$$+ \varepsilon^2 \sum_{\alpha'} |<\alpha|\Lambda_1|\alpha'>|^2 \{\frac{(\lambda_\alpha-\lambda_{\alpha'})F'(\lambda_\alpha)-(F(\lambda_\alpha)-F(\lambda_{\alpha'}))}{(\lambda_\alpha-\lambda_{\alpha'})^2}\} + O(\varepsilon^2).$$

Now, writing the free energy and Hamiltonian as:

$$\phi = \phi_o + \varepsilon\phi_1 + \varepsilon^2\phi_2 + \ldots; \quad H = H_o + \varepsilon H_1$$

and making the following choices and definitions:

$$\Lambda \equiv \phi - H \; ; \; \Lambda_o \equiv \phi_o - H_o \; ; \quad \varepsilon\Lambda_1 = \varepsilon(\phi_1 - H_1) + \varepsilon^2\phi_2 + \ldots$$

$$F(\lambda) = e^{\beta\Lambda} = e^{\beta(\phi-H)} \; ; \; \lambda_\alpha = \phi_o - E_\alpha \; ; \quad \beta = (k_B T)^{-1}$$

we obtain, upon collecting powers of ε:

$$<\alpha|e^{\beta(\phi-H)}|\alpha> = e^{\beta(\phi_o-E_\alpha)} + \varepsilon<\alpha|(\phi_1 - H_1)|\alpha> e^{\beta\lambda_\alpha}$$

$$+ \varepsilon^2\Big[<\alpha|\phi_2|\alpha>\beta e^{\beta\lambda_\alpha} + \sum_{\alpha'} |<\alpha|(\phi_1-H_1)|\alpha'>|^2 \times$$

$$\times \{\frac{\beta(\lambda_\alpha-\lambda_{\alpha'})e^{\beta\lambda_\alpha} - (e^{\beta\lambda_\alpha} - e^{\beta\lambda_{\alpha'}})}{(\lambda_\alpha-\lambda_{\alpha'})^2}\}\Big] + O(\varepsilon^3) \; .$$

Then, applying the condition:

$$Tr[e^{\beta(\phi-H)}] = Tr[e^{\beta(\phi_o-H_o)}] = 1$$

and equating coefficients of powers of ε, we obtain:

$$\phi_1 = \sum_\alpha \langle\alpha|H_1|\alpha\rangle e^{\beta(\phi_o-E_\alpha)}$$

$$(1.1)\quad \phi_2 = \frac{\beta}{2}\phi_1^2 - \sum_{\alpha,\alpha'} |\langle\alpha|H_1|\alpha'\rangle|^2 \times$$

$$\times\left\{\frac{\beta(\lambda_\alpha-\lambda_{\alpha'})e^{\beta\lambda_\alpha} - (e^{\beta\lambda_\alpha} - e^{\beta\lambda_{\alpha'}})}{(\lambda_\alpha-\lambda_{\alpha'})^2}\right\}$$

$$= \frac{\beta}{2}\phi_1^2 - \sum_{\alpha,\alpha'} |\langle\alpha|H_1|\alpha'\rangle|^2 \left\{\frac{e^{\beta\lambda_\alpha} - e^{\beta\lambda_{\alpha'}}}{2(\lambda_\alpha-\lambda_{\alpha'})}\right\}$$

$$= \frac{\beta}{2}\phi_1^2 + \sum_{\alpha,\alpha'} |\langle\alpha|H_1|\alpha'\rangle|^2 \left\{\frac{1 - e^{\beta(E_\alpha-E_{\alpha'})}}{2(E_\alpha-E_{\alpha'})}\right\} e^{\beta(\phi_o-E_\alpha)}.$$

§1.2 Hamiltonian

The Hamiltonian for this problem is given by:

$$(1.2)\quad H = H_I(\underset{\sim}{R}) + \sum_i \frac{p_i^2}{2m} + \sum_i H_{int}(\underset{\sim}{r}_i, \underset{\sim}{R})$$

where $\underset{\sim}{r}_i$ and $\underset{\sim}{p}_i$ are the position and momentum coordinates of the i^{th} conduction electron, and the symbol $\underset{\sim}{R}$ denotes the set of all ionic coordinates, including momenta when necessary. H_I describes the ionic system

in the absence of interaction with the conduction electrons. For the general formalism, it is not necessary to specify this operator, and thus the final results will be applicable to a wide class of ionic systems.

The pseudopotential interaction for an electron at position $\underset{\sim}{r}$ is defined by its action on an arbitrary wave function $\eta(\underset{\sim}{r})$:

$$H_{int}(\underset{\sim}{r},\underset{\sim}{R})\eta(\underset{\sim}{r}) = \sum_j v_j^{local}(\underset{\sim}{r}-\underset{\sim}{R}_j)\eta(\underset{\sim}{r})$$

$$+ \sum_j \sum_{c_j} B_{c_j} \psi_{c_j}(\underset{\sim}{r}-\underset{\sim}{R}_j) \int d\underset{\sim}{r}' \psi^*_{c_j}(\underset{\sim}{r}'-\underset{\sim}{R}_j)\eta(\underset{\sim}{r}')$$

where ψ_{c_j} is the wave function of the c_j^{th} core level of the ion at $\underset{\sim}{R}_j$. Note that $\underset{\sim}{R}_j$ is the actual position of the j^{th} ion, and not the j^{th} site on a perfect lattice.

The effects of electronic screening of the ions, as well as any direct interactions between the conduction electrons are assumed to have been already incorporated into H_{int} by a preliminary calculation.

It will be found useful to transform this Hamiltonian, using the second quantization scheme for the electrons, and to combine the "diagonal" part of the interaction term with the kinetic energy of the unperturbed electron gas. Thus, we may make use of the

following prescription for a "one-electron" operator $\overleftrightarrow{\alpha}$ [19]:

$$\overleftrightarrow{\alpha} \equiv \sum_i \overleftrightarrow{\alpha}(\underset{\sim}{r}_i) \rightarrow \sum_{\underset{\sim}{k},\underset{\sim}{k}'} \langle \underset{\sim}{k}' | \alpha(\underset{\sim}{r}) | \underset{\sim}{k} \rangle C^\dagger_{\underset{\sim}{k}'} C_{\underset{\sim}{k}}$$

where $|\underset{\sim}{k}\rangle$ is the plane wave state of a free electron having momentum $\hbar\underset{\sim}{k}$, and $C^\dagger_{\underset{\sim}{k}}$ and $C_{\underset{\sim}{k}}$ are the Fermi creation and annihilation operators. The Hamiltonian (1.2) then becomes:

$$H = H_I + \sum_{\underset{\sim}{k}} C^\dagger_{\underset{\sim}{k}} C_{\underset{\sim}{k}} \left(\frac{\hbar^2 k^2}{2m}\right) + \sum_{\underset{\sim}{k},\underset{\sim}{k}'} C^\dagger_{\underset{\sim}{k}'} C_{\underset{\sim}{k}} A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})$$

$$= H_I + \sum_{\underset{\sim}{k}} C^\dagger_{\underset{\sim}{k}} C_{\underset{\sim}{k}} E_{\underset{\sim}{k}} + \sum'_{\underset{\sim}{k},\underset{\sim}{k}'} C^\dagger_{\underset{\sim}{k}'} C_{\underset{\sim}{k}} A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})$$

$$\equiv H_o + H_1 \ .$$

The prime on the summation indicates that the $\underset{\sim}{k} = \underset{\sim}{k}'$ terms are omitted, and the following definitions are used:

$$(1.3) \quad H_o = H_I + \sum_{\underset{\sim}{k}} C^\dagger_{\underset{\sim}{k}} C_{\underset{\sim}{k}} E_{\underset{\sim}{k}} \ ; \quad H_1 = \frac{1}{N} \sum'_{\underset{\sim}{k},\underset{\sim}{k}'} C^\dagger_{\underset{\sim}{k}'} C_{\underset{\sim}{k}} A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})$$

$$A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R}) = \sum_j e^{i(\underset{\sim}{k}-\underset{\sim}{k}')\cdot\underset{\sim}{R}_j} W_j(\underset{\sim}{k},\underset{\sim}{k}')$$

$$(1.4) \quad W_j(\underset{\sim}{k},\underset{\sim}{k}') = \frac{N}{V} \int d\underset{\sim}{r}\, e^{i(\underset{\sim}{k}-\underset{\sim}{k}')\cdot\underset{\sim}{r}} v_j^{\text{local}}(\underset{\sim}{r})$$

$$+ \frac{N}{V} \sum_{c_j} B_{c_j} \int d\underset{\sim}{r}\, e^{i\underset{\sim}{k}'\cdot\underset{\sim}{r}} \psi_{c_j}(r) \int d\underset{\sim}{r}' \psi^*_{c_j}(\underset{\sim}{r}') e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}'}$$

$$(1.5) \quad E_{\underset{\sim}{k}} = \frac{\hbar^2 k^2}{2m} + A_{\underset{\sim}{k}} \quad ; \quad A_{\underset{\sim}{k}} \equiv \sum_j W_j(\underset{\sim}{k},\underset{\sim}{k}) \ .$$

In the general case $W_j(\underset{\sim}{k},\underset{\sim}{k}')$, and thus $A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})$, depend on both $\underset{\sim}{k}$ and $\underset{\sim}{k}'$ separately, due to the non-locality of the pseudopotential. In simpler circumstances, where non-local effects may be safely ignored, W_j becomes a function of $\underset{\sim}{q} \equiv \underset{\sim}{k} - \underset{\sim}{k}'$ only, and is just equal to the Fourier transform of the local part of the interaction. That is,

$$W_j(\underset{\sim}{k},\underset{\sim}{k}') \to W_j(\underset{\sim}{q}) = \frac{N}{V} \int d\underset{\sim}{r} \, e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}} \, v_j^{\text{local}}(\underset{\sim}{r}) \ .$$

In this case, $A_{\underset{\sim}{k}} \to A_o = \sum_j W_j(0)$, which is just a constant, equal to the average value of the interaction, and simply shifts the zero of energy for the electrons. We will use this approximation in the numerical calculation in Chapter 4, but for the general development, the full non-local form will be used.

As might be supposed, the eigenvalue problem for H_o is considered to have been already solved, and H_1 will be regarded as a perturbation.

1.3 Expression for Free Energy

Now, the eigenstates $\{|\alpha\rangle\}$ of the unperturbed system can be written as direct products of ionic states

$\{|n>\}$ and the many-body states of the electron gas,

$$|\alpha> = |n>|\sigma_{\underset{\sim}{k}_1}\ \sigma_{\underset{\sim}{k}_2}\ \ldots\ \sigma_{\underset{\sim}{k}_m}\ \ldots> \ ; \quad \sigma_{\underset{\sim}{k}_m} = 0 \text{ or } 1$$

and with H_1 as given by (1.3), we have immediately that,

$$<\alpha|H_1|\alpha> = 0 \ , \ \text{+} \quad \phi_1 = 0 \ .$$

Thus the first non-zero correction to ϕ_o will come in second order, remembering, of course, that ϕ_o refers to an unperturbed system, the electron gas part of which has the "modified" energy levels given by (1.5).

In the second order term (1.1), the matrix elements of the perturbation may be calculated in the following manner:

$$<\alpha'|H_1|\alpha> = \frac{1}{N}<n'|<\sigma'|\sum_{\underset{\sim}{k},\underset{\sim}{k}'} C^{\dagger}_{\underset{\sim}{k}'}C_{\underset{\sim}{k}}A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})|\sigma>|n>$$

$$= \frac{1}{N}\sum_{\underset{\sim}{k},\underset{\sim}{k}'} <n'|A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})|n><\sigma'|C^{\dagger}_{\underset{\sim}{k}'},C_{\underset{\sim}{k}}|\sigma>$$

$$<\sigma'|C^{\dagger}_{\underset{\sim}{k}'},C_{\underset{\sim}{k}}|\sigma> = \sigma'_{\underset{\sim}{k}_1}\sigma'_{\underset{\sim}{k}_2}\ldots\sigma'_{\underset{\sim}{k}'}\sigma'_{\underset{\sim}{k}'}\ldots|C^{\dagger}_{\underset{\sim}{k}'},C_{\underset{\sim}{k}}|\sigma_{\underset{\sim}{k}_1}\sigma_{\underset{\sim}{k}_2}\ldots\sigma_{\underset{\sim}{k}}\sigma_{\underset{\sim}{k}'}\ldots>$$

$$= \sigma_{\underset{\sim}{k}}(1-\sigma_{\underset{\sim}{k}'})\delta_{\sigma'_{\underset{\sim}{k}_1}\sigma'_{\underset{\sim}{k}_2}}\ldots\sigma'_{\underset{\sim}{k}'}\sigma'_{\underset{\sim}{k}'}\ldots|\sigma_{\underset{\sim}{k}_1}\sigma_{\underset{\sim}{k}_2}\ldots(\sigma_{\underset{\sim}{k}}-1),(\sigma_{\underset{\sim}{k}'}+1),\ldots>$$

$$= \sigma_{\underset{\sim}{k}}(1-\sigma_{\underset{\sim}{k}'})\delta_{\sigma'_{\underset{\sim}{k}_1}\sigma_{\underset{\sim}{k}_2}}\delta_{\sigma'_{\underset{\sim}{k}_2}\sigma_{\underset{\sim}{k}_2}}\ldots\delta_{\sigma'_{\underset{\sim}{k}_1}(\sigma_{\underset{\sim}{k}}-1)}\delta_{\sigma'_{\underset{\sim}{k}_1}(\sigma_{\underset{\sim}{k}'}+1)}\ldots.$$

Using this result, we then have

$$|\langle\alpha'|H_1|\alpha\rangle|^2 = \frac{1}{N^2} \sum_{\underset{\sim}{k},\underset{\sim}{k}'\ \underset{\sim}{\ell},\underset{\sim}{\ell}'} \langle n'|A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})|n\rangle\langle n|A(\underset{\sim}{\ell},\underset{\sim}{\ell}';\underset{\sim}{R})|n'\rangle \cdot$$

$$\cdot \sigma_{\underset{\sim}{k}}(1-\sigma_{\underset{\sim}{k}'})\sigma_{\underset{\sim}{\ell}}(1-\sigma_{\underset{\sim}{\ell}'}) \cdot$$

$$\cdot \delta_{\sigma'_{\underset{\sim}{k}_1}\sigma_{\underset{\sim}{k}_1}} \delta_{\sigma'_{\underset{\sim}{k}_2}k_2} \cdots \delta_{\sigma'_{\underset{\sim}{\ell}}\sigma_{\underset{\sim}{\ell}}} \delta_{\sigma_{\underset{\sim}{\ell}'}\sigma_{\underset{\sim}{\ell}'}} \cdots \delta_{\sigma_{\underset{\sim}{k}},(\sigma_{\underset{\sim}{k}}-1)} \delta_{\sigma_{\underset{\sim}{k}'},(\sigma_{\underset{\sim}{k}'}+1)} \cdots$$

$$\cdot \delta_{\sigma'_{\underset{\sim}{k}_1}\sigma_{\underset{\sim}{k}_1}} \delta_{\sigma_{\underset{\sim}{k}_2}\sigma_{\underset{\sim}{k}_2}} \cdots \delta_{\sigma_{\underset{\sim}{\ell}},(\sigma_{\underset{\sim}{\ell}}-1)} \delta_{\sigma_{\underset{\sim}{\ell}'},(\sigma_{\underset{\sim}{\ell}'}+1)} \cdots \delta_{\sigma'_{\underset{\sim}{k}}\sigma_{\underset{\sim}{k}}} \delta_{\sigma_{\underset{\sim}{k}'}\sigma_{\underset{\sim}{k}'}} \cdots$$

Now, the string of Kronecker deltas can be non-zero only if $\underset{\sim}{\ell} = \underset{\sim}{k}$ and $\underset{\sim}{\ell}' = \underset{\sim}{k}'$. Then, remembering that $\sigma_{\underset{\sim}{k}}^2 = \sigma_{\underset{\sim}{k}}$ and $(1-\sigma_{\underset{\sim}{k}})^2 = (1-\sigma_{\underset{\sim}{k}})$, because of the fact that $\sigma_{\underset{\sim}{k}} = 0$ or 1, we obtain:

$$|\langle\alpha'|H_1|\alpha\rangle|^2 = \frac{1}{N^2} \sum_{k,k'} |\langle n'|A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})|n\rangle|^2 \, \sigma_{\underset{\sim}{k}}(1-\sigma_{\underset{\sim}{k}'}) \cdot$$

$$\cdot \{\sigma_{\sigma'_{\underset{\sim}{k}_1}\sigma_{\underset{\sim}{k}_1}} \delta_{\sigma_{\underset{\sim}{k}_2}\sigma_{\underset{\sim}{k}_2}} \cdots \delta_{\sigma'_{\underset{\sim}{k}},(\sigma_{\underset{\sim}{k}}-1)} \delta_{\sigma'_{\underset{\sim}{k}_1},(\sigma_{\underset{\sim}{k}_1}+1)} \cdots\} \cdot$$

Now, with $E_\alpha = E_n + \sum_{\underset{\sim}{k}} \sigma_{\underset{\sim}{k}} E_{\underset{\sim}{k}}$, we can rewrite $e^{\beta(\phi_o - E_\alpha)}$ as a product of statistical factors for the ions and electrons:

$$e^{\beta(\phi_o - E_\alpha)} = e^{\beta((\phi_o^{\text{ion}} - E_n) + (\phi_o^{\text{electron}} - \sum_{\underset{\sim}{k}} \sigma_{\underset{\sim}{k}} E_{\underset{\sim}{k}})}$$

$$\equiv P_n \, P\{\sigma_{\underset{\sim}{k}}\}$$

where p_n is the probability of finding the ions in state $|n\rangle$ and $p_{\{\sigma_k\}}$ in the probability of finding the electron gas with the set of occupation numbers $\{\sigma_k\}$.

Using these results in (1.1), we obtain the following expression for ϕ_2:

$$\phi_2 = \frac{1}{N^2} \sum_{n,n',\{\sigma_{\underset{\sim}{k}}\},\{\sigma'_{\underset{\sim}{k}}\}} p_n p_{\{\sigma_{\underset{\sim}{k}}\}} \left(\frac{1-e^{\beta((E_n-E_{n'})+\sum_{\underset{\sim}{k}}(\sigma_{\underset{\sim}{k}}-\sigma'_{\underset{\sim}{k}})E_{\underset{\sim}{k}})}}{2((E_n-E_{n'})+\sum_{\underset{\sim}{k}}(\sigma_{\underset{\sim}{k}}-\sigma'_{\underset{\sim}{k}})E_{\underset{\sim}{k}})} \right)$$

$$\cdot \sum'_{\underset{\sim}{k},\underset{\sim}{k}'} |\langle n'|A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})|n\rangle|^2 \sigma_{\underset{\sim}{k}}(1-\sigma_{\underset{\sim}{k}'})\delta_{\sigma'_{\underset{\sim}{k}},(\sigma_{\underset{\sim}{k}}-1)}\delta_{\sigma'_{\underset{\sim}{k}'},\sigma_{\underset{\sim}{k}'}+1}$$

$$\cdot \prod''_m \delta_{\sigma'_{\underset{\sim}{k}_m},\sigma_{\underset{\sim}{k}_m}}$$

where the double prime on the product indicates that the terms $\underset{\sim}{k}_m = \underset{\sim}{k}$ and $\underset{\sim}{k}'$ are omitted. Now, doing the sum over $\{\sigma'_{\underset{\sim}{k}}\}$ first, the only non-zero terms are given by:

$$\sum_{\sigma'_{\underset{\sim}{k}}=0}^{1} \sum_{\sigma'_{\underset{\sim}{k}'}=0}^{1} \frac{1-e^{\beta((E_n-E_{n'})+(\sigma_{\underset{\sim}{k}}-\sigma'_{\underset{\sim}{k}})E_{\underset{\sim}{k}}+(\sigma_{\underset{\sim}{k}'}-\sigma'_{\underset{\sim}{k}'})E_{\underset{\sim}{k}'})}}{2((E_n-E_{n'})+(\sigma_{\underset{\sim}{k}}-\sigma'_{\underset{\sim}{k}})E_{\underset{\sim}{k}}+(\sigma_{\underset{\sim}{k}'}-\sigma'_{\underset{\sim}{k}'})E_{\underset{\sim}{k}'})}$$

$$\cdot \delta_{\sigma'_{\underset{\sim}{k}},(\sigma_{\underset{\sim}{k}}-1)}\delta_{\sigma'_{\underset{\sim}{k}'},\sigma_{\underset{\sim}{k}'}+1}$$

$$= \frac{1-e^{\beta((E_n-E_{n'})+(E_{\underset{\sim}{k}}-E_{\underset{\sim}{k}'}))}}{2((E_n-E_{n'})+(E_{\underset{\sim}{k}}-E_{\underset{\sim}{k}'}))} \cdot$$

This gives

$$\phi_2 = \frac{1}{N^2} \sum_{n,n'} \sum_{\underset{\sim}{k},\underset{\sim}{k}'}' \left[p_n \frac{1 - e^{\beta((E_n - E_{n'}) + (E_{\underset{\sim}{k}} - E_{\underset{\sim}{k}'}))}}{2((E_n - E_{n'}) + (E_{\underset{\sim}{k}} - E_{\underset{\sim}{k}'}))} \right]$$

$$\cdot |\langle n'|A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})|n\rangle|^2 \sum_{\{\sigma_{\underset{\sim}{k}}\}} p_{\{\sigma_{\underset{\sim}{k}}\}} \sigma_{\underset{\sim}{k}} (1-\sigma_{\underset{\sim}{k}'}) \ .$$

Then, noting that $\sum_{\{\sigma_{\underset{\sim}{k}}\}} p_{\{\sigma_{\underset{\sim}{k}}\}} \sigma_{\underset{\sim}{k}} = \langle \sigma_{\underset{\sim}{k}} \rangle = f_{\underset{\sim}{k}}$, the Fermi distribution; and including a factor of 2 for the two possible spin states, we have:

$$(1.6) \qquad \phi_2 = \frac{1}{N^2} \sum_{\underset{\sim}{k},\underset{\sim}{k}'}' f_{\underset{\sim}{k}}(1-f_{\underset{\sim}{k}'}) \sum_{n,n'} p_n |\langle n'|A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})|n\rangle|^2$$

$$\cdot \left[\frac{1 - e^{\beta\hbar(\omega_{\underset{\sim}{k}\underset{\sim}{k}'} - \omega_{n'n})}}{\hbar(\omega_{\underset{\sim}{k}\underset{\sim}{k}'} - \omega_{n'n})} \right]$$

where $\hbar\omega_{\underset{\sim}{k}\underset{\sim}{k}'} = (E_{\underset{\sim}{k}} - E_{\underset{\sim}{k}'})$, and $\hbar\omega_{n'n} = (E_{n'} - E_n)$.

Now, define a function $\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega)$ as follows:

$$(1.7) \qquad \Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega) = \frac{1}{N} \sum_{n,n'} p_n |\langle n'|A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})|n\rangle|^2 \delta(\omega - \omega_{n'n})$$

$$= \int \frac{dt}{2\pi N} \sum_{n,n'} p_n e^{-i(\omega - \omega_{n'n})t} |\langle n'|A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})|n\rangle|^2$$

$$= \int \frac{dt}{2\pi N} e^{-i\omega t} \sum_{n,n'} p_n \langle n|A^\dagger(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})|n'\rangle\langle n'|e^{\frac{i}{\hbar}H_I t} A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})$$

$$\cdot e^{-\frac{i}{\hbar}H_I t}|n\rangle$$

$$= \int \frac{dt}{2\pi N} e^{-i\omega t} \sum_{n} p_n \langle n|A^\dagger(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R}(0))A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R}(t))|n\rangle$$

$$\equiv \int \frac{dt}{2\pi N} e^{-i\omega t} \langle A^\dagger(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R}(0))A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R}(t))\rangle_T \ .$$

Here $\underset{\sim}{R}(t)$ represents the Heisenberg position operators of the unperturbed ionic system, and thus we have:

$$(1.8)\quad A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R}(t)) = \sum_j W_j(\underset{\sim}{k},\underset{\sim}{k}')\, e^{i(\underset{\sim}{k}-\underset{\sim}{k}')\cdot\underset{\sim}{R}_j(t)}$$

$$\underset{\sim}{R}_j(t) = e^{\frac{i}{\hbar}H_I t}\, \underset{\sim}{R}_j(0)\, e^{-\frac{i}{\hbar}H_I t} \quad .$$

Next, note that using (1.7), we have:

$$\int_{-\infty}^{\infty} d\omega \left(\frac{\beta\hbar(\omega_{\underset{\sim}{k}\underset{\sim}{k}'},-\omega)}{1 - e^{\hbar(\omega_{\underset{\sim}{k}\underset{\sim}{k}'},-\omega)}} \right) \Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega)$$

$$= \frac{1}{N} \sum_{n,n'} p_n |\langle n'|A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})|n\rangle|^2 \left(\frac{\beta\hbar(\omega_{\underset{\sim}{k}\underset{\sim}{k}'},-\omega_{n'n})}{1-e^{\hbar(\omega_{\underset{\sim}{k}\underset{\sim}{k}'},-\omega_{n'n})}} \right)$$

and combining this result with (1.6) gives,

$$(1.9)\quad \phi_2 = \frac{1}{N} \sum_{\underset{\sim}{k}}{}' \sum_{\underset{\sim}{k}'} f_{\underset{\sim}{k}}(1-f_{\underset{\sim}{k}'}) \int_{-\infty}^{\infty} d\omega \left(\frac{\beta\hbar(\omega_{\underset{\sim}{k}\underset{\sim}{k}'},-\omega)}{1-e^{\hbar(\omega_{\underset{\sim}{k}\underset{\sim}{k}'},-\omega)}} \right) \Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega) .$$

This relation can be further simplified with the help of a few easily obtained relations. From (1.4), we see that $W_j^*(\underset{\sim}{k}',\underset{\sim}{k}) = W_j(\underset{\sim}{k},\underset{\sim}{k}')$, and thus,

$$A^\dagger(\underset{\sim}{k}',\underset{\sim}{k};\underset{\sim}{R}) = A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R}) \quad .$$

Then, from the definition (1.7), and using (1.8),

$$\Gamma(\underset{\sim}{k}',\underset{\sim}{k},-\omega) = \frac{1}{N}\sum_{nn'} P_n |\langle n'|A(\underset{\sim}{k}',\underset{\sim}{k};\underset{\sim}{R})|n\rangle|^2 \delta(\omega+\omega_{n',n})$$

$$= \frac{1}{N}\sum_{nn'} P_{n'} |\langle n|A(\underset{\sim}{k}',\underset{\sim}{k};\underset{\sim}{R})|n\rangle|^2 \delta(\omega-\omega_{n',n})$$

$$= e^{-\beta\hbar\omega}\frac{1}{N}\sum_{nn'} P_n |\langle n|A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R})|n'\rangle|^2 \delta(\omega-\omega_{n',n})$$

and from (1.7), we thus obtain,

$$(1.10) \qquad \Gamma(\underset{\sim}{k}',\underset{\sim}{k},-\omega) = e^{-\beta\hbar\omega}\,\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega) \quad .$$

It is also readily seen that:

$$(1.11) \qquad f_{\underset{\sim}{k}'}(1-f_{\underset{\sim}{k}}) = \left(\frac{1}{e^{\beta(E_{\underset{\sim}{k}'}-\mu)}+1}\right)\left(\frac{e^{\beta(E_{\underset{\sim}{k}}-\mu)}}{e^{\beta(E_{\underset{\sim}{k}}-\mu)}+1}\right)$$

$$= \left(\frac{e^{\beta(E_{k'}-\mu)}}{e^{\beta(E_{\underset{\sim}{k}'}-\mu)}+1}\right)\left(\frac{e^{\beta(E_k-E_{k'})}}{e^{\beta(E_{\underset{\sim}{k}}-\mu)}+1}\right)$$

$$= e^{\beta\hbar\omega_{\underset{\sim}{k}\underset{\sim}{k}'}}\, f_{\underset{\sim}{k}}(1-f_{\underset{\sim}{k}'}) \quad .$$

Then, for that part of ϕ_2 arising from the second term in the integrand of (1.9), we may obtain, using (1.10) and (1.11),

$$\sum_{\underset{\sim}{k},\underset{\sim}{k}'} f_{\underset{\sim}{k}}(1-f_{\underset{\sim}{k}'}) \, \mathcal{P}\int_{-\infty}^{\infty} d\omega \, \frac{e^{\beta\hbar(\omega_{\underset{\sim}{k}\underset{\sim}{k}'},-\omega)}}{(\omega_{\underset{\sim}{k}\underset{\sim}{k}'},-\omega)} \, \Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega)$$

$$= -\sum_{\underset{\sim}{k},\underset{\sim}{k}'}{}' f_{\underset{\sim}{k}'}(1-f_{\underset{\sim}{k}}) \, \mathcal{P}\int_{-\infty}^{\infty} d\omega \, \frac{e^{-\beta\hbar(\omega_{\underset{\sim}{k}\underset{\sim}{k}'},+\omega)}}{(\omega_{\underset{\sim}{k}\underset{\sim}{k}'},+\omega)} \, \Gamma(\underset{\sim}{k}',\underset{\sim}{k},\omega)$$

$$= -\sum_{\underset{\sim}{k},\underset{\sim}{k}'}{}' f_{\underset{\sim}{k}'}(1-f_{\underset{\sim}{k}}) \, \mathcal{P}\int_{-\infty}^{\infty} d\omega \, \frac{e^{-\beta\hbar(\omega_{\underset{\sim}{k}\underset{\sim}{k}'},-\omega)}}{(\omega_{\underset{\sim}{k}\underset{\sim}{k}'},-\omega)} \, \Gamma(\underset{\sim}{k}',\underset{\sim}{k},-\omega)$$

$$= -\sum_{\underset{\sim}{k},\underset{\sim}{k}'}{}' f_{\underset{\sim}{k}}(1-f_{\underset{\sim}{k}'}) \, \mathcal{P}\int_{-\infty}^{\infty} d\omega \, \frac{\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega)}{(\omega_{\underset{\sim}{k}\underset{\sim}{k}'},-\omega)}$$

where $\mathcal{P}$ indicates that the principal value of the integral is to be taken. This term gives exactly the same contribution to the free energy as the first term, and thus we finally obtain [20],

$$(1.12) \qquad \phi_2 = \frac{2}{N} \sum_{\underset{\sim}{k},\underset{\sim}{k}'} f_{\underset{\sim}{k}}(1-f_{\underset{\sim}{k}'}) \int_{-\infty}^{\infty} d\omega \, \frac{\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega)}{\hbar(\omega_{\underset{\sim}{k}\underset{\sim}{k}'},-\omega)} \, .$$

This formula is the central result of this work, and will figure prominently in what is to follow. It is applicable to solid or liquid metals and alloys, including those whose constituents have different mass and volume; and it allows for arbitrary dynamical properties of the ionic system. The essential limitation is that the electron-ion interaction must be adequately

described by local or non-local pseudopotentials of the type defined by equation (1.4).

Any contributions from elastic Bragg scattering should be excluded from (1.12), since these are related to the original band structure, and thus belong with the modified zero-order results. Other than this, (1.12) gives all the second order corrections to the free energy, and, by deduction, to such properties as the specific heat.

Now, from the form of (1.12), it is apparent that $\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega)$ contains all the information that is needed for a particular case, and thus the determination of this function will be of primary importance. We shall, therefore, discuss Γ in some detail, beginning with the work in which a similar type of function was just used in the literature.

CHAPTER 2

DYNAMICAL STRUCTURE FACTORS

§2.1 Introductory Remarks

In 1954, Van Hove [9] examined the problem of the inelastic scattering of thermal neutrons in a pure substance. For this case, the interaction is well represented by a "local" approximation, and will be the same for one ion as for any other; that is, $W_j(\underset{\sim}{q}) = W(\underset{\sim}{q})$ for all j. If one calculates the cross-section for the inelastic scattering of a neutron from a state of wave-vector $\underset{\sim}{k}$ to a state $\underset{\sim}{k}'$, in the Born approximation, then the result may be expressed in the form,

$$(2.1) \qquad \frac{d^2\sigma}{d\Omega dE} = \text{const } \left(\frac{k'}{k}\right) \Gamma(\underset{\sim}{q},\omega_{\underset{\sim}{k}\underset{\sim}{k}'})$$

$$(2.2) \qquad \Gamma(\underset{\sim}{q},\omega_{\underset{\sim}{k}\underset{\sim}{k}'}) = |W(\underset{\sim}{q})|^2 \, S(\underset{\sim}{q},\omega_{\underset{\sim}{k}\underset{\sim}{k}'})$$

where $S(\underset{\sim}{q},\omega)$ is the Van Hove dynamical structure factor. This function is the space-time Fourier transform of the time-dependent, quantum-mechanical pair distribution function for the ions, and may be written as:

$$S(\underset{\sim}{q},\omega) = \int \frac{dt}{2\pi N} e^{-i\omega t} \left\langle \sum_j e^{-i\underset{\sim}{q}\cdot\underset{\sim}{R}_j(0)} \sum_{j'} e^{i\underset{\sim}{q}\cdot\underset{\sim}{R}_{j'}(t)} \right\rangle_T$$

where $\langle \ldots \rangle_T$ indicates an ensemble average over the unperturbed ionic system.

Now, the case of conduction electrons in a metal, being scattered by the ions, can be treated in the same way in the pseudopotential framework, and one obtains a result which is identical with (2.1), except that $\Gamma(\underset{\sim}{q},\omega_{kk'})$ is replaced by $\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega)$ as given by (1.7).

The separation of Γ into atomic and structural factors, as given by (2.2) in the case of a pure substance in the local limit, is indicative of a more general state of affairs. In the case of an arbitrary ν-component alloy, with non-local effects, we will show presently that $\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega)$ may be written as a sum of terms similar to (2.2), involving ν different pseudopotentials and ν^2 dynamical structure factors (DSF's). In most cases, indeed in all cases, if the pseudopotentials are taken to be real, the number of DSF's may be reduced to $\nu(\nu+1)/2$. These functions will be found to depend on $\underset{\sim}{k}$ and $\underset{\sim}{k}'$, only through the combination $\underset{\sim}{q} = \underset{\sim}{k} - \underset{\sim}{k}'$, while the separate $\underset{\sim}{k}$ and $\underset{\sim}{k}'$ dependence which signifies non-local effects, will be confined to the pseudopotentials $W_j(\underset{\sim}{k},\underset{\sim}{k}')$.

An important feature of being able to separate $\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega)$ into "form factors" and "structure factors" is that it allows, at least in principle, for the

experimental determination of the DSF's. If one knows the interaction potentials for neutron scattering in a solid say, then using Van Hove's results (or their extension to alloys), one should be able to obtain the DSF's from an analysis of thermal neutron scattering data.

Once the DSF's have been determined for a particular system, they may be then used to study any scattering problem in that system. One need only know the appropriate matrix elements of the interaction, and thus form $\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega)$. Having done this, one may proceed directly to calculate such things as free energy and specific heat corrections from (1.12), or the electrical resistivity of an alloy, which may be expressed as a different integral of the same scattering function [21].

§2.2 α-α' Structure Factors

The structure factors of an alloy are closely connected to the operators which describe the local number density of each constituent as a function of time; and one may express the DSF's directly in terms of these operators, in a manner similar to the procedure of Van Hove.

Thus, for a ν-component alloy, with each type of ion labelled by an index $\alpha = 1,2,\ldots,\nu$, we may write

the local number density of type α as:

$$(2.3) \qquad n_\alpha(\underset{\sim}{r},t) = \sum_j^{(\alpha)} \delta(\underset{\sim}{r}-\underset{\sim}{R}_j^{(\alpha)}(t))$$

where the superscripted (α) indicates that the sum is only carried out over this type of atom. The space Fourier transform of this operator is then given by

$$(2.4) \qquad N_\alpha(\underset{\sim}{q},t) = \int d\underset{\sim}{r}\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}}\, n_\alpha(\underset{\sim}{r},t)$$

$$= \sum_j^{(\alpha)} e^{i\underset{\sim}{q}\cdot\underset{\sim}{R}_j^{(\alpha)}(t)}$$

and using (1.8), we may thus write,

$$(2.5) \qquad A(\underset{\sim}{k},\underset{\sim}{k}',\underset{\sim}{R}(t)) = \sum_\alpha W_\alpha(\underset{\sim}{k},\underset{\sim}{k}')N_\alpha(\underset{\sim}{q},t)$$

it being assumed that within an alloy of given composition, each ion of a particular type carries the same self-consistent potential, denoted here by $W_\alpha(\underset{\sim}{k},\underset{\sim}{k}')$.

Now, using (2.5) and (1.7), and suppressing the wave-vector dependence of W_α and N_α for the time being, we may write Γ as,

$$\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega) = \int \frac{dt}{2\pi N} e^{-i\omega t} \langle \sum_\alpha W_\alpha^* N_\alpha^\dagger(0) \sum_{\alpha'} W_{\alpha'} N_{\alpha'}(t) \rangle_T \quad .$$

Then, upon adding and subtracting terms involving

$N_{\alpha}^{\dagger}, (0) N_{\alpha}(t)$, we may rewrite Γ as,

$$(2.6) \qquad \Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega) = \sum_{\alpha,\alpha'} W_{\alpha}^{*} W_{\alpha'} (S_{\alpha\alpha'}(\underset{\sim}{q},\omega) + S_{\alpha\alpha'}^{(a)}(\underset{\sim}{q},\omega))$$

where we have defined the DSF's

$$(2.7) \qquad S_{\alpha\alpha'}(\underset{\sim}{q},\omega) = \int \frac{dt}{4\pi N} e^{-i\omega t} \langle N_{\alpha}^{\dagger}(\underset{\sim}{q},0) N_{\alpha'}(\underset{\sim}{q},t) + N_{\alpha}^{\dagger}(\underset{\sim}{q},0) N_{\alpha}(\underset{\sim}{q},t) \rangle_{T}$$

$$(2.8) \qquad S_{\alpha\alpha'}^{(a)}(\underset{\sim}{q},\omega) = \int \frac{dt}{4\pi N} e^{-i\omega t} \langle N_{\alpha}^{\dagger}(\underset{\sim}{q},0) N_{\alpha'}(\underset{\sim}{q},t) - N_{\alpha}^{\dagger}(\underset{\sim}{q},0) N_{\alpha}(\underset{\sim}{q},t) \rangle_{T} \quad .$$

We may note that since $n_{\alpha}(\underset{\sim}{r},t)$ is real valued, then equation (2.4) implies that $N_{\alpha}^{\dagger}(\underset{\sim}{q},t) = N_{\alpha}(-\underset{\sim}{q},t)$. Thus, from (2.7) and (2.8), we may see that the $S_{\alpha\alpha'}$ are real-valued and symmetric (with respect to interchange of α and α'), while the $S_{\alpha\alpha'}^{(a)}$ are anti-symmetric and pure imaginary. Thus if the pseudopotentials are real, or at least satisfy $W_{\alpha} = |W_{\alpha}| e^{i\gamma}$, where γ is the same for all α, then the contributions from the terms involving $S_{\alpha\alpha'}^{(a)}$ are zero. Moreover, as Bhatia [22] has pointed out, because of the ensemble average in the definition (2.8), the symmetry of most systems would require that $S_{\alpha\alpha'}^{(a)} = 0$.

At any rate, we shall not include the anti-symmetric terms, and thus obtain,

$$\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega) = \sum_{\alpha,\alpha'} W^{*}_{\alpha}(\underset{\sim}{k},\underset{\sim}{k}')W_{\alpha'}(\underset{\sim}{k},\underset{\sim}{k}')S_{\alpha\alpha'}(\underset{\sim}{q},\omega) \quad . \tag{2.9}$$

This method of writing Γ is simple and direct, since it gives the de-composition in terms of the correlations between the positions of the different types of ions which make up the alloy. There are other ways of constructing Γ however, and one may define different, but equivalent sets of DSF's, which might have the effect of accentuating some physical features of particular interest, or which may be more easily related to some experimental data. By choosing the proper set, it may also be possible to reduce the number of structure factors needed, if some parameter, such as the ionic volume, for example, is roughly the same for all the constituents.

§2.3 N-C Structure Factors (Binary Alloys)

For a binary alloy, Bhatia and Thornton [21] introduced a set of three DSF's which express the dynamics of the alloy in an instructive manner. They wrote Γ as,

$$\Gamma(\underset{\sim}{q},\omega) = (\bar{W})^2 S_{NN}(\underset{\sim}{q},\omega) + (W_1-W_2)^2 S_{CC}(\underset{\sim}{q},\omega) + 2\bar{W}(W_1-W_2) S_{NC}(\underset{\sim}{q},\omega) \tag{2.10}$$

where $\bar{W} = c_1 W_1 + c_2 W_2$, and c_α is the concentration of type α. S_{NN} is quite similar to the single structure factor of a pure substance, and describes the correlations between the fluctuations in particle density. S_{CC} describes the correlations between concentration fluctuations, and S_{NC} is the cross-correlation between the two.

These DSF's will be properly defined later on, but for the moment we may make a few over-simplified remarks about the physical significance of the different parts of (2.10). The first term represents a "dynamic virtual crystal" contribution, in which the ionic vibrations are taken into account, while the second term arises basically from an "electron-impurity" interaction. This latter term may be often well represented by the "static approximation", in which its frequency dependence is given by a factor $\delta(\omega)$. The third term reflects predominantly those effects which owe their origins to differences in size and shape between the two types of ions. It will be generally negligible if

they have close to the same volume, thus leaving only two independent DSF's in such cases.

In a paper subsequent to [21], Bhatia and Thornton [23] derived exact expressions for the high-temperature, long-wavelength ($\underset{\sim}{q} \sim 0$) limit of the "static" structure factors ($S_{NN}(\underset{\sim}{q}) = \int d\omega\, S_{NN}(\underset{\sim}{q},\omega)$ etc.), from fluctuation theory. For the case of a cubic crystal, the explicit expressions are:

$$S_{NN}(\hat{y}) = \left(\frac{N}{V}\right) k_B T \kappa(\hat{y}) + \left[\frac{S_{NC}(\hat{y})}{S_{CC}(\hat{y})}\right]^2 S_{CC}(\hat{y})$$

$$S_{CC}(\hat{y}) = \frac{Nk_B T}{\left(\frac{\partial^2 \mathcal{G}}{\partial c_1^2}\right)_{T,\sigma,N} + V\delta^2 B_T (1 - B_T \kappa(\hat{y}))}$$

$$S_{NC}(\hat{y}) = -\delta B_T \kappa(\hat{y}) S_{CC}(\hat{y})$$

where $\hat{y}$ is a unit vector in the direction of $\underset{\sim}{q}$ (remembering that $|\underset{\sim}{q}| \sim 0$), $\mathcal{G}$ is the Gibbs free energy, B_T is the isothermal bulk modulus, c_1 is the concentration of species 1, and σ is the stress tensor. $\kappa(\hat{y})$ is given by the expression

$$\kappa(\hat{y}) = \sum_{\xi=1}^{3} \frac{(\hat{y}\cdot\hat{e}_{y,\xi})^2}{\rho v_{y,\xi}^2}$$

where $\hat{e}_{y,\xi}$ is the (unit) polarization vector for a wave propagating along $\hat{y}$ with velocity $v_{y,\xi}$, and ρ is the density of the substance. The symbol δ is defined as

$$\frac{1}{3}\,\delta = e_{11} = e_{22} = e_{33}$$

where $e_{ii} = (\partial\varepsilon_{ii}/\partial c_1)_{T,\sigma,N}$, with ε being the strain tensor. If the strains introduced by the differing volumes of the alloyed species are quite small, then δ is closely equal to $(v_1-v_2)/(c_1v_1+c_2v_2)$, where v_i is the molar volume of species i. Thus one readily sees that the requirement for S_{NC} to be zero in this case is essentially that $v_1 = v_2$, as we have mentioned above. We also note that for this case

$$S_{CC} = \frac{Nk_BT}{\frac{\partial^2 g}{\partial c^2}}$$

and thus for a random alloy $S_{CC} = c(1-c)$.

For shorter wavelengths (larger $\underset{\sim}{q}$), exact expressions are not available (in explicit form) for these structure factors, but as noted in [23], one may obtain some qualitative information from the results of X-ray scattering theory, which essentially deals with the static structure factors. In particular, one may deduce

from the works of Huang [24] and Krivoglaz [25] that for an elastically isotropic random alloy,

$$\frac{S_{NC}(\underset{\sim}{q})}{S_{CC}(\underset{\sim}{q})} \approx \frac{\delta \cdot B_T}{c_{11}} \frac{\underset{\sim}{q} \cdot (\underset{\sim}{G} - \underset{\sim}{q})}{|\underset{\sim}{G} - \underset{\sim}{q}|^2}$$

where G is the reciprocal lattice vector closest to $\underset{\sim}{q}$, and c_{11} is one of the elastic constants. We may note that this expression is again equal to zero for $v_1 = v_2$.

In addition, we see that this result becomes infinite for $\underset{\sim}{q} = \underset{\sim}{G}$, and one would thus expect large contributions to any quantity involving S_{NC} for values of $\underset{\sim}{q}$ in this region. We will encounter similar behaviour in Chapter 4 when we consider the umklapp contributions to the electronic specific heat. The principal difference is that for the present case we have (for $\underset{\sim}{q}$ parallel to $\underset{\sim}{G}$):

$$S_{NC} \propto \frac{q}{(G - q)}$$

while in Chapter 4 we will have (loosely speaking):

$$S_{NN} \propto \frac{q^2}{(G - q)^2}$$

which is a stronger effect, but of the same type nevertheless.

§2.4 N-C Structure Factors (ν-Component Alloys)

Now, proceeding to the case of a ν-component alloy, we may follow Bhatia and Thornton, and relate the DSF's to the fluctuations in the local number density of the alloyed species, rather than the full number density. In fact, if one describes the local fluctuations of type α by,

$$\delta n_\alpha(\underset{\sim}{r},t) = n_\alpha(\underset{\sim}{r},t) - \bar{n}_\alpha$$

$$N_\alpha(\underset{\sim}{q},t) = \int d\underset{\sim}{r}\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}}\, n_\alpha(\underset{\sim}{r},t)$$

$$= \sum_j^{(\alpha)} e^{i\underset{\sim}{q}\cdot\underset{\sim}{R}_j^{(\alpha)}(t)} - N_\alpha\, \delta_{\underset{\sim}{q},o}$$

where $\bar{n}_\alpha = N_\alpha/V$, and further recognizes that elastic forward scattering ($\underset{\sim}{k} = \underset{\sim}{k}'$) has no effect on the structure-dependent electron-ion processes, then the preceding development, from (2.3) to (2.9), goes through exactly as before, except that there are a lot of terms involving $\delta_{\underset{\sim}{q},o} = \delta_{\underset{\sim}{k},\underset{\sim}{k}'}$, which are simply ignored.

Now, in order to construct a set of DSF's which reduce to S_{NN}, S_{NC}, and S_{CC} in the binary case, we will define an operator which describes the fluctuations in local concentration of a given species by,

$$\delta c_\alpha(\underset{\sim}{r},t) = (V/N)(\delta n_\alpha(\underset{\sim}{r},t) - c_\alpha \delta n(\underset{\sim}{r},t))$$

where $\delta n(\underset{\sim}{r},t) = \sum_\alpha \delta n_\alpha(\underset{\sim}{r},t)$ is the operator describing the total fluctuation in number density, and $c_\alpha = N_\alpha/N$. The Fourier transform of $\delta c_\alpha(\underset{\sim}{r},t)$ is given by,

$$(2.11) \quad C_\alpha(\underset{\sim}{q},t) = (\tfrac{1}{V}) \int d\underset{\sim}{r}\, e^{i\underset{\sim}{q}.\underset{\sim}{r}} \delta c_\alpha(\underset{\sim}{r},t)$$

$$= (\tfrac{1}{N})(N_\alpha(\underset{\sim}{q},t) - c_\alpha N(\underset{\sim}{q},t))$$

with $N(\underset{\sim}{q},t) = \sum_\alpha N_\alpha(\underset{\sim}{q},t)$. Also note that,

$$(2.12) \quad \sum_\alpha c_\alpha(\underset{\sim}{r},t) = \sum_\alpha C_\alpha(\underset{\sim}{q},t) = 0 \ .$$

Now, using (2.11), we may write,

$$N_\alpha(\underset{\sim}{q},t) = NC_\alpha(\underset{\sim}{q},t) + c_\alpha N(\underset{\sim}{q},t)$$

and thus, from (2.5), we have,

$$A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R}(t)) = \bar{W}(\underset{\sim}{k},\underset{\sim}{k}')N(\underset{\sim}{q},t) + N \sum_\alpha W_\alpha(\underset{\sim}{k},\underset{\sim}{k}')C_\alpha(\underset{\sim}{q},t)$$

with $\bar{W}(\underset{\sim}{k},\underset{\sim}{k}') \equiv \sum_\alpha c_\alpha W_\alpha(\underset{\sim}{k},\underset{\sim}{k}')$.

In case of a binary alloy ($\alpha = 1,2$), we see from (2.12) that $C_1(\underset{\sim}{q},t) = -C_2(\underset{\sim}{q},t) \equiv C(\underset{\sim}{q},t)$, and that we may thus write,

$$A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R}(t)) = \bar{W}N(\underset{\sim}{q},t) + N(W_1 - W_2)C(\underset{\sim}{q},t) \ .$$

In the general case also, it will often be advantageous

to work in terms of differences, rather than full pseudopotentials, and thus, taking advantage of (2.12), we may write

$$A(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{R}(t)) = \bar{W}N(\underset{\sim}{q},t) + N\sum_{\alpha}(W_\alpha - W_\nu)C_\alpha(\underset{\sim}{q},t)$$

where ν may represent any one of the alloyed species. Using this relation in (1.7), we then obtain,

$$(2.13)\quad \Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega) = \int\frac{dt}{2\pi N}e^{-i\omega t}\langle\{\bar{W}^*\bar{W}N^\dagger(\underset{\sim}{q},0)N(\underset{\sim}{q},t)$$

$$+ N^2\sum_{\alpha,\alpha'}(W_\alpha^* - W_\nu^*)(W_{\alpha'} - W_\nu)C_\alpha^\dagger(\underset{\sim}{q},0)C_{\alpha'}(\underset{\sim}{q},t)$$

$$+ N\sum_{\alpha}(\bar{W}^*(W_\alpha - W_\nu)N^\dagger(\underset{\sim}{q},0)C_\alpha(\underset{\sim}{q},t) + \bar{W}(W_\alpha^* - W_\nu^*)C_\alpha^\dagger(\underset{\sim}{q},0)N(\underset{\sim}{q},t))\}\rangle_T.$$

Then, following the same type of argument that preceded (2.9), we may "symmetrize" this form of Γ, and obtain,

$$(2.14)\quad \Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega) = |\bar{W}|^2 S_{NN}(\underset{\sim}{q},\omega) + \sum_{\alpha,\alpha'}(W_\alpha^* - W_\nu^*)(W_{\alpha'} - W_\nu)\times$$

$$\times S_{C_\alpha C_{\alpha'}}(\underset{\sim}{q},\omega)$$

$$+\sum_{\alpha}[\bar{W}^*(W_\alpha - W_\nu) + \bar{W}(W_\alpha^* - W_\nu^*)]S_{NC_\alpha}(\underset{\sim}{q},\omega)$$

where we have defined,

$$(2.15a)\quad S_{NN}(\underset{\sim}{q},\omega) = \int\frac{dt}{2\pi N}e^{-i\omega t}\langle N^\dagger(\underset{\sim}{q},0)N(\underset{\sim}{q},t)\rangle_T$$

$$(2.15b)\quad S_{C_\alpha C_\alpha}(\underset{\sim}{q},\omega) = \frac{N^2}{2}\int \frac{dt}{2\pi N}\, e^{-i\omega t}\langle C_\alpha^\dagger(\underset{\sim}{q},0)C_\alpha(\underset{\sim}{q},t) + C_\alpha^\dagger(\underset{\sim}{q},0)C_\alpha(\underset{\sim}{q},t)\rangle_T$$

$$(2.15c)\quad S_{NC_\alpha}(\underset{\sim}{q},\omega) = \frac{N}{2}\int \frac{dt}{2\pi N}\, e^{-i\omega t}\langle N^\dagger(\underset{\sim}{q},0)C_\alpha(\underset{\sim}{q},t) + C_\alpha^\dagger(\underset{\sim}{q},0)N(\underset{\sim}{q},t)\rangle_T \ .$$

By expressing $C_\alpha(\underset{\sim}{q},t)$ and $N(\underset{\sim}{q},t)$ in terms of the $N_\alpha(\underset{\sim}{q},t)$, one may easily verify that going from (2.13) to (2.14) is exactly equivalent to the progression from (2.6) to (2.9), and that one result implies the other.

Just as there are $\nu(\nu+1)/2$ independent DSF's of the $S_{\alpha\alpha'}$ type, there are the same number in the set of number-concentration DSF's, of which

1 is of the (NN) type,

$(\nu-1)$ are of the (NC) type,

$\frac{\nu(\nu-1)}{2}$ are of the (CC) type.

One may also, of course, write a given set of structure factors as a linear combination of any other properly defined set; and for the two types just given, we have,

$$S_{\alpha\alpha'}(\underset{\sim}{q},\omega) = c_\alpha c_{\alpha'} S_{NN}(\underset{\sim}{q},\omega) + S_{C_\alpha C_{\alpha'}}(\underset{\sim}{q},\omega) + c_\alpha S_{NC_{\alpha'}}(\underset{\sim}{q},\omega) + c_{\alpha'} S_{NC_\alpha}(\underset{\sim}{q},\omega)$$

and the inverse relations,

$$S_{NN}(\underset{\sim}{q},\omega) = \sum_{\alpha,\alpha'} S_{\alpha\alpha'}(\underset{\sim}{q},\omega)$$

$$S_{NC_\alpha}(\underset{\sim}{q},\omega) = \sum_{\alpha',\alpha''} (\delta_{\alpha'\alpha} - c_\alpha) S_{\alpha'\alpha''}(\underset{\sim}{q},\omega)$$

$$S_{C_\alpha C_{\alpha'}}(\underset{\sim}{q},\omega) = \sum_{\alpha'',\alpha'''} (\delta_{\alpha''\alpha} - c_\alpha)(\delta_{\alpha'''\alpha'} - c_{\alpha'}) S_{\alpha''\alpha'''}(\underset{\sim}{q},\omega)$$

from which it is apparent that

$$\sum_\alpha S_{NC_\alpha}(\underset{\sim}{q},\omega) = \sum_\alpha S_{C_\alpha C_{\alpha'}}(\underset{\sim}{q},\omega) = 0$$

as is required by (2.12) and the definitions (2.15). This is simply a statement of the fact that, while there are localized fluctuations throughout the substance, the total number of ions is fixed.

§2.5 Structure Factors for a Substitutional Alloy

Although one might hope for progress in the experimental determination of the DSF's, it is at present a difficult undertaking to attempt accurate theoretical calculations of these functions. Nevertheless, it is still possible to obtain useful insight into many physically interesting processes by considering somewhat idealized situations.

One such example, which we shall make use of later on, is that of a substitutional alloy. The basic assumption operating in this case is that one may interchange ions of the various species at random, without causing significant changes in the local ionic structure. This implies a certain degree of uniformity in size and shape, of course, but is not entirely unrealistic. One knows experimentally that it is difficult to form homogeneous alloys from constituents which differ markedly from one another in this respect, the Hume-Rothery 15% rule [26] being the classic indicator. This rule states that if the constituents differ from one another by more than about 15% in linear dimensions, then their mutual solubility will be severely restricted (i.e. to less than about 5%).

In order to introduce the degree of randomness required in this case, we take the probability that a given position in the alloy is occupied by an ion of type α as being equal to c_α, the concentration of that species in the alloy. We thus obtain the configurational average:

$$(2.16)\quad \overline{W_j^* W_{j'}} = \delta_{jj'} \sum_\alpha c_\alpha W_\alpha^* W_\alpha + (1-\delta_{jj'}) \sum_\alpha c_\alpha W_\alpha^* \sum_\alpha c_\alpha W_\alpha$$

$$= \left| \sum_\alpha c_\alpha W_\alpha \right|^2 + \delta_{jj'} \left\{ \sum_\alpha c_\alpha |W_\alpha|^2 - \left| \sum_\alpha c_\alpha W_\alpha \right|^2 \right\} .$$

This result may be cast into a variety of equivalent forms, and for present purposes, in order to facilitate comparison with (2.14), we introduce the pseudopotential differences $(W_\alpha - W_\nu)$, and obtain

$$\overline{W_j^* W_{j'}} = \left|\sum_\alpha c_\alpha W_\alpha\right|^2 + \delta_{jj'} \, \mathrm{Re} \sum_{\alpha,\alpha'} c_\alpha (\delta_{\alpha'\alpha} - c_{\alpha'}) (W_\alpha^* - W_\nu^*)(W_{\alpha'} - W_\nu).$$

Then, writing $\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega)$ explicitly as

$$\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega) = \int \frac{dt}{2\pi N} e^{-i\omega t} \Big\langle \sum_{jj'} W_j^* W_{j'} e^{-i\underset{\sim}{q}\cdot\underset{\sim}{R}_j(0)} e^{i\underset{\sim}{q}\cdot\underset{\sim}{R}_{j'}(t)} \Big\rangle_T \tag{2.17}$$

and replacing $W_j^* W_{j'}$ by $\overline{W_j^* W_{j'}}$ from (2.16), we have

$$\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega) = |\bar{W}|^2 S_{NN}(\underset{\sim}{q},\omega) \tag{2.18}$$

$$+ \{\mathrm{Re} \sum_{\alpha,\alpha'} c_\alpha (\delta_{\alpha'\alpha} - c_{\alpha'}) (W_\alpha^* - W_\nu^*)(W_{\alpha'} - W_\nu)\} S_I(\underset{\sim}{q},\omega)$$

where $S_{NN}(\underset{\sim}{q},\omega)$ and $S_I(\underset{\sim}{q},\omega)$ are given by

$$S_{NN}(\underset{\sim}{q},\omega) = \int \frac{dt}{2\pi N} e^{-i\omega t} \Big\langle \sum_{jj'} e^{-i\underset{\sim}{q}\cdot\underset{\sim}{R}_j(0)} e^{i\underset{\sim}{q}\cdot\underset{\sim}{R}_{j'}(t)} \Big\rangle_T$$

$$S_I(\underset{\sim}{q},\omega) = \int \frac{dt}{2\pi N} e^{-i\omega t} \Big\langle \sum_{j} e^{-i\underset{\sim}{q}\cdot\underset{\sim}{R}_j(0)} e^{i\underset{\sim}{q}\cdot\underset{\sim}{R}_j(t)} \Big\rangle_T . \tag{2.19}$$

$S_{NN}(\underset{\sim}{q},\omega)$, as defined here, is exactly the same as (2.15a), of course, and by comparing the forms of (2.14) and (2.18), we may deduce that

$$S_{NC_\alpha}(\underset{\sim}{q},\omega) = 0 \quad \text{for all } \alpha$$

which means that the fluctuations in number density and concentration are independent of one another, as might be expected from the discussion of §2.3 and the assumption of no lattice distortion in the present case. In addition, we see that

$$S_{C_\alpha C_{\alpha'}}(\underset{\sim}{q},\omega) = c_\alpha(\delta_{\alpha'\alpha} - c_{\alpha'})S_I(\underset{\sim}{q},\omega)$$

which shows that the concentration fluctuations are all correlated through the same dynamical behaviour, with each contribution to the scattering being weighted by the concentrations of the various species, and by the relative strengths of the pseudopotentials. Thus in this simplified case one has only two independent structure factors to deal with.

The first and second terms in (2.18) correspond exactly to the "coherent" and "incoherent" scattering cross-sections that one encounters in the current treatment of thermal neutron scattering [25]. Indeed, one may see from (2.16) that the coefficient of $S_I(\underset{\sim}{q},\omega)$ is just $(\overline{W^2} - \bar{W}^2)$, which is the form more commonly seen in neutron scattering theory. The W's are different, of course, but the form is the same, and the structure factors are exactly the same, as has been stated earlier.

CHAPTER 3

APPLICATIONS

§3.1 Preliminary Remarks

For a given system, represented by its appropriate pseudopotentials and DSF's in the scattering function $\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega)$, expression (1.12) gives a straightforward prescription for calculating the second order corrections to the free energy. A significant aspect of this result is that it embodies, in a simple concise expression, many results which are usually treated quite separately from one another, using different techniques. These techniques are often difficult to extend without a complete reformulation, while (1.12), within the basic limitations discussed earlier, is very general.

As illustrative examples, we shall consider a number of representative cases, which will serve to demonstrate the utility of this formula.

§3.2 Harmonic Solid

As a first example, let us approximate a pure metal by a system of ions executing harmonic vibrations about equilibrium positions on a perfect lattice, which is the usual "phonon" model.

In this case, the Hamiltonian is given by

$$H_I = \sum_s \hbar\omega_s (a_s^\dagger a_s + \tfrac{1}{2})$$

where s indicates one of the 3N vibrational modes of the crystal. This index may be further written as $s \equiv (\underset{\sim}{Q},\xi)$, with each of the N wave-vectors ($\underset{\sim}{Q}$) corresponding to three polarization modes ($\xi = 1,2,3$), having unit vectors $\hat{e}_s$ and frequencies ω_s. The Bose creation and annihilation operators, $a_s^\dagger$ and a_s, satisfy the commutation relation

$$[a_s, a_{s'}^\dagger] = \delta_{ss'} \quad .$$

Then if $\underset{\sim}{x}_j$ is the j^{th} ionic site on the perfect lattice, we may write

$$\underset{\sim}{R}_j(t) = \underset{\sim}{x}_j + \underset{\sim}{u}_j(t)$$

where $\underset{\sim}{u}_j(t)$ is given by the standard theory [27] as

$$(3.1) \qquad \underset{\sim}{u}_j(t) = \sum_s \left(\frac{\hbar}{2NM\omega_s}\right)^{\frac{1}{2}} \hat{e}_s \{a_s e^{-i(\omega_s t - \underset{\sim}{Q}\cdot\underset{\sim}{x}_j)} + a_s^\dagger e^{i(\omega_s t - \underset{\sim}{Q}\cdot\underset{\sim}{x}_j)}\}$$

with M as the ionic mass. From (3.1) we may readily deduce that

$$\theta_{j',j}(\underset{\sim}{q},t) \equiv [-i\underset{\sim}{q}\cdot\underset{\sim}{u}_j(0), i\underset{\sim}{q}\cdot\underset{\sim}{u}_{j'}(t)]$$

$$= \frac{i\hbar}{NM} \sum_s (\underset{\sim}{q}\cdot\hat{e}_s)^2 \left[\frac{\sin(\omega_s t - \underset{\sim}{Q}\cdot(\underset{\sim}{x}_{j'} - \underset{\sim}{x}_j))}{\omega_s}\right]$$

which is an ordinary c-number. Thus we may write

$$\langle e^{-i\underset{\sim}{q}\cdot\underset{\sim}{R}_j(0)} e^{i\underset{\sim}{q}\cdot\underset{\sim}{R}_{j'}(t)} \rangle_T = e^{i\underset{\sim}{q}\cdot(\underset{\sim}{x}_{j'}-\underset{\sim}{x}_j)} \langle e^{-i\underset{\sim}{q}\cdot\underset{\sim}{u}_j(0)} e^{i\underset{\sim}{q}\cdot\underset{\sim}{u}_{j'}(t)} \rangle_T$$

$$= e^{i\underset{\sim}{q}\cdot(\underset{\sim}{x}_{j'}-\underset{\sim}{x}_j)} e^{\frac{1}{2}\theta_{j,j'}(\underset{\sim}{q},t)} \langle e^{i\underset{\sim}{q}\cdot(\underset{\sim}{u}_{j'}(t)-\underset{\sim}{u}_j(0))} \rangle_T$$

where we have used the common identity $e^A e^B = e^{A+B} e^{\frac{1}{2}[A,B]}$, which is valid if $[A,[A,B]] = [B,[A,B]] = 0$.

The exponent of the term to be averaged can be thus seen as a simple sum over phonon states, with each term commuting with every other term. Then, since we may write an ionic state, in this approximation, as $|n\rangle = \prod_s |n_s\rangle$, where $a_s^\dagger |n_s\rangle = (n_s+1)^{\frac{1}{2}} |n_s+1\rangle$ etc., the average becomes a product over all modes of terms of the form

$$\langle e^{i(\gamma_s a_s + \gamma_s^* a_s^\dagger)} \rangle_T = e^{-\frac{1}{2}\gamma_s^*\gamma_s(2\bar{n}_s+1)} \tag{3.2}$$

(see Messiah [28]), where $\bar{n}_s = (e^{\beta\hbar\omega_s} - 1)^{-1}$, and in the present case, we have

$$\gamma_s = \left(\frac{\hbar}{2NM\omega_s}\right)(\underset{\sim}{q}\cdot\hat{\underset{\sim}{e}}_s)(e^{-i(\omega_s t - \underset{\sim}{Q}\cdot\underset{\sim}{x}_{j'})} - e^{i\underset{\sim}{Q}\cdot\underset{\sim}{x}_j}) .$$

Using this result in (3.2), we obtain

$$(3.3)\quad \langle e^{-i\underset{\sim}{q}\cdot\underset{\sim}{R}_j(0)}\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{R}_{j'}(t)}\rangle_T = e^{i\underset{\sim}{q}\cdot(\underset{\sim}{x}_j,-\underset{\sim}{x}_{j'})}\cdot$$

$$e^{\sum_s \frac{\hbar(\underset{\sim}{q}\cdot\hat{\underset{\sim}{e}}_s)^2}{2NM\omega_s}\{(\bar{n}_s+1)e^{i(\omega_s t-\underset{\sim}{Q}\cdot(\underset{\sim}{x}_j,-\underset{\sim}{x}_{j'}))}+\bar{n}_s e^{-i(\omega_s t-\underset{\sim}{Q}\cdot(\underset{\sim}{x}_j,-\underset{\sim}{x}_{j'}))}-(2\bar{n}_s+1)\}}.$$

We must then insert this into formula (2.17) in order to obtain $\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega)$. Because of the difficulty in performing the time integrations, however, one may resort to the procedure of expanding the second factor in a power series and performing the integrations term by term. Then, making use of the fact that

$$\sum_{j,j'} e^{i\underset{\sim}{q}\cdot(\underset{\sim}{x}_j,-\underset{\sim}{x}_{j'})} = N^2 \sum_{\underset{\sim}{G}} \delta_{\underset{\sim}{q},\underset{\sim}{G}}$$

where $\underset{\sim}{G}$ is a vector of the reciprocal lattice, we keep only first order terms in the expansion and thus obtain the "one phonon approximation":

$$(3.4)\quad \Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega) = N|W(\underset{\sim}{k},\underset{\sim}{k}')|^2 \sum_{\underset{\sim}{G}}\{\delta(\omega)\delta_{\underset{\sim}{q},\underset{\sim}{G}}\cdot$$

$$(1-\sum_s \frac{\hbar(\underset{\sim}{q}\cdot\hat{\underset{\sim}{e}}_s)^2}{2NM\omega_s}(2\bar{n}_s+1)) + \sum_s \frac{\hbar(\underset{\sim}{q}\cdot\hat{\underset{\sim}{e}}_s)^2}{2NM\omega_s}((\bar{n}_s+1)\delta(\omega-\omega_s)\delta_{\underset{\sim}{q}-\underset{\sim}{Q},\underset{\sim}{G}}$$

$$+ \bar{n}_s\delta(\omega+\omega_s)\delta_{\underset{\sim}{q}+\underset{\sim}{Q},\underset{\sim}{G}})\}$$

$$+ |W(\underset{\sim}{k},\underset{\sim}{k}')|^2 \sum_{\underset{\sim}{G},s} \frac{\hbar(\underset{\sim}{q}\cdot\hat{\underset{\sim}{e}}_s)^2}{2M\omega_s}((\bar{n}_s+1)\delta(\omega-\omega_s) + \bar{n}_s\delta(\omega+\omega_s))\delta_{\underset{\sim}{q}-\underset{\sim}{Q},\underset{\sim}{G}}$$

where we have dropped the elastic Bragg terms ($\delta_{\underset{\sim}{q},\underset{\sim}{G}}$) in line with the remarks made earlier, and used $(\underset{\sim}{q}\cdot\hat{e}_{\underset{\sim}{Q},\xi})^2 = (\underset{\sim}{q}\cdot\hat{e}_{-\underset{\sim}{Q},\xi})^2$.

The higher order, or "multi-phonon", terms in the expansion of (3.3) may be obtained directly, but we will confine ourselves here to first order. One point to be noticed, however, is that the "Debye-Waller factor"

$$e^{-2D(\underset{\sim}{q})} \equiv e^{-\sum_s \frac{\hbar(\underset{\sim}{q}\cdot\hat{e}_s)^2}{2NM\omega_s}(2\bar{n}_s+1)}$$

need not be expanded for the purpose of performing the time integrations, and may thus be left in exponential form, as is the practice in X-ray scattering problems. But there have been arguments to the effect that this term and the time-dependent terms may substantially cancel one another in higher orders [29]. This matter remains somewhat unsettled, however, and for present purposes we will adopt the policy of expanding (3.3) consistently to the same order in the exponent, treating the Debye-Waller part in the same way as the rest.

Note that using the definition of $\bar{n}_s$, and the relation $f(a)\delta(x-a) = f(x)\delta(x-a)$, we may rewrite (3.4) in the alternate forms

$$\Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega) = \frac{|W(\underset{\sim}{k},\underset{\sim}{k}')|^2}{|\omega|(1-e^{-\beta\hbar\omega})} \sum_{G,s} \frac{\hbar(\underset{\sim}{q}\cdot\hat{\underset{\sim}{e}}_s)^2}{2M}(\delta(\omega-\omega_s)-\delta(\omega+\omega_s))\delta_{\underset{\sim}{q}-\underset{\sim}{Q},\underset{\sim}{G}}$$

$$= \left(\frac{\omega}{|\omega|}\right)\frac{2|W(\underset{\sim}{k},\underset{\sim}{k}')|^2}{(1-e^{-\beta\hbar\omega})} \sum_{G,s} \frac{\hbar(\underset{\sim}{q}\cdot\hat{\underset{\sim}{e}}_s)^2}{2M} \delta(\omega^2-\omega_s^2)\delta_{\underset{\sim}{q}-\underset{\sim}{Q},\underset{\sim}{G}}$$

which are sometimes useful for calculations.

Inserting (3.4) into (1.12) and performing the frequency integrations gives for the free energy correction

$$(3.5)\quad \phi_2 = 2\sum_{\underset{\sim}{k},\underset{\sim}{k}'}{}' \sum_{\underset{\sim}{G},s} \frac{(\underset{\sim}{q}\cdot\hat{\underset{\sim}{e}}_s)^2}{2NM\omega_s}|W(\underset{\sim}{k},\underset{\sim}{k}')|^2\delta_{\underset{\sim}{q}-\underset{\sim}{Q},\underset{\sim}{G}} \cdot$$

$$\left[\frac{(\bar{n}_s+1)f_{\underset{\sim}{k}}(1-f_{\underset{\sim}{k}'}) - \bar{n}_s f_{\underset{\sim}{k}'}(1-f_{\underset{\sim}{k}})}{\omega_{\underset{\sim}{k}\underset{\sim}{k}'} - \omega_s}\right] .$$

This is a more complete version of the expression used by Buckingham and Schafroth [10] in their specific heat calculations. In their case the Umklapp ($\underset{\sim}{G} \neq 0$) terms were dropped, an isotropic Debye model was used for the phonons, and the factor $|W(\underset{\sim}{k},\underset{\sim}{k}')|^2(\underset{\sim}{q}\cdot\hat{\underset{\sim}{e}}_s)^2/2M\omega_s$ was replaced by a simplified "interaction parameter" which varied linearly with $|\underset{\sim}{Q}|$.

Expression (3.5) may be separated into two terms, one of which depends only on "virtual" phonon processes, while the other depends directly on the phonon occupation numbers. This gives

$$(3.6)\qquad \phi_2 = 2 \sum_{\underset{\sim}{k},\underset{\sim}{k}'}{}' \sum_{\underset{\sim}{G},s} \frac{(\underset{\sim}{q}\cdot\hat{\underset{\sim}{e}}_s)^2}{2NM\omega_s} |W(\underset{\sim}{k},\underset{\sim}{k}')|^2 \delta_{\underset{\sim}{q}-\underset{\sim}{Q},\underset{\sim}{G}} \left(\frac{f_{\underset{\sim}{k}}(1-f_{\underset{\sim}{k}'})}{\omega_{\underset{\sim}{k}\underset{\sim}{k}'}-\omega_s} \right)$$

$$+ 2 \sum_{\underset{\sim}{k},\underset{\sim}{k}'} \sum_{\underset{\sim}{G},s} \frac{(\underset{\sim}{q}\cdot\hat{\underset{\sim}{e}}_s)^2}{2NM\omega_s} |W(\underset{\sim}{k},\underset{\sim}{k}')|^2 \delta_{\underset{\sim}{q}-\underset{\sim}{Q},\underset{\sim}{G}} \left(\frac{2\omega_{\underset{\sim}{k}\underset{\sim}{k}'}}{\omega^2_{\underset{\sim}{k}\underset{\sim}{k}'} - \omega_s^2} \right) f_{\underset{\sim}{k}} \bar{n}_s$$

where it is understood that the sums will eventually be converted to integrals and principal values taken when the singularities present problems.

The second term is zero at $T = 0$, and does not contribute to the electronic specific heat coefficient. It may be interpreted as representing a renormalization of the speed of sound. The first term in (3.6) will yield the "electron-phonon enhancement" of the electronic specific heat, which is finite at $T = 0$, and becomes zero at high temperatures, as discussed in §0.4. (See [10] and [15]).

§3.3 Liquid Metal

Beyond the melting point of a metal, there will be some degree of short-range order, but there is no regular lattice, and such concepts as band structure and Bragg reflections are no longer applicable. In such circumstances, the scattering function must include all elastic and inelastic processes. Indeed, the elastic processes will tend to dominate the scattering to a

large extent, since they may no longer be assigned to the band structure. This fact makes it easy to obtain a good first approximation to the electronic properties of liquid metals.

In setting up an expression for the electrical resistivity of a metallic substance, using the current variational approach, one finds that the scattering function enters in an integral of the form

$$(3.7) \qquad I(\underset{\sim}{q}) = \int_{-\infty}^{\infty} d\omega \left(\frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1}\right) \Gamma(\underset{\sim}{q},\omega)$$

in the local pseudopotential approximation [21]. Thus at liquid metal temperatures, and for the range of energies accessible to the system,

$$\beta\hbar\omega << 1 \ , \quad \text{and} \quad I(\underset{\sim}{q}) \cong \int_{-\infty}^{\infty} d\omega \ \Gamma(\underset{\sim}{q},\omega) \ .$$

In the case at hand, we are dealing with the same scattering processes that are responsible for the resistivity, and in the same approximation, we may use

$$S(\underset{\sim}{q},\omega) \cong S(\underset{\sim}{q}) \ \delta(\omega)$$

where $S(\underset{\sim}{q})$ is the "static" structure factor, $S(\underset{\sim}{q}) = \int d\omega \ S(\underset{\sim}{q},\omega)$, which gives the total scattering in a given direction $\underset{\sim}{q}$. Using this relation in (1.12), we obtain

$$(3.8)\qquad \phi_2 = \frac{2}{N}\mathcal{P}\sum_{\underset{\sim}{k},\underset{\sim}{k}'}{}' |W(\underset{\sim}{k},\underset{\sim}{k}')|^2\, S(\underset{\sim}{q})\, \frac{f_{\underset{\sim}{k}}(1-f_{\underset{\sim}{k}'})}{E_{\underset{\sim}{k}} - E_{\underset{\sim}{k}'}}$$

$$= \frac{2}{N}\mathcal{P}\sum_{k,k'}{}' |W(\underset{\sim}{k},\underset{\sim}{k}')|^2\, S(\underset{\sim}{q})\, \frac{f_{\underset{\sim}{k}}}{E_{\underset{\sim}{k}} - E_{\underset{\sim}{k}'}}$$

which may be written as

$$(3.9)\qquad \phi_2 = 2\int dE_{\underset{\sim}{k}}\, n_o(E_{\underset{\sim}{k}}) f_{\underset{\sim}{k}}\, G(E_{\underset{\sim}{k}})$$

where

$$G(E_{\underset{\sim}{k}}) = \frac{1}{N}\mathcal{P}\int\frac{d\Omega_{\underset{\sim}{k}}}{4\pi}\int\frac{d\Omega_{\underset{\sim}{k}'}}{4\pi}\, dE_{\underset{\sim}{k}'} n_o(E_{\underset{\sim}{k}'})\, \frac{|W(\underset{\sim}{k},\underset{\sim}{k}')|^2 S(\underset{\sim}{q})}{E_{\underset{\sim}{k}} - E_{\underset{\sim}{k}'}}$$

and $n_o(E_k) = (V/(2\pi)^3)\, 4\pi k^2/(dE_{\underset{\sim}{k}}/dk)$ is the density of states, for each spin, of the "modified" free electron gas, with $E_{\underset{\sim}{k}}$ given by (1.5) as $E_{\underset{\sim}{k}} = (\hbar^2 k^2/2m) + A_{\underset{\sim}{k}}$.

Assuming that the liquid metal is still much below the "Fermi temperature", we may expand (3.9) in the usual manner [1], and obtain for the first two terms:

$$(3.10)\qquad \phi_2 = 2\int_0^{\mu_o} dE_k n_o(E_k) G(E_k) + \frac{\pi^2}{3}(k_B T)^2 n_o(\mu_o) G'(\mu_o)$$

where μ_o is the chemical potential at $T = 0$, and $G'(\mu_o) = [dG(E_k)/dE_k]_{E_{\underset{\sim}{k}}=\mu_o}$.

The second term in (3.10) gives a correction to the specific heat, according to the formula $\Delta C_V = -T(\partial^2\phi_2/\partial T^2)_V$, which is

$$(3.11) \qquad \Delta C_V/C_V^e = -G'(\mu_o)$$

with $C_V^e = \frac{2}{3}\pi^2 k_B^2 n_o(\mu_o)T$ as the specific heat of the free electron gas. In view of the high temperature, however, this correction will be completely dominated by other effects, and may be safely ignored.

The first term, however, is of more interest. It is seen to be independent of temperature, and since the total energy is equal to the free energy at T = 0, we may, in view of the form of (3.8), interpret this term as a correction to the electron energy. Thus we write the energy of an electron in a state $\underset{\sim}{k}$, to second order, as

$$\varepsilon(\underset{\sim}{k}) = E_{\underset{\sim}{k}} + \frac{1}{N}\mathcal{P}\sum_{\underset{\sim}{k}'} \frac{|W(\underset{\sim}{k},\underset{\sim}{k}')|^2 S(\underset{\sim}{q})}{(E_{\underset{\sim}{k}} - E_{\underset{\sim}{k}'})} \quad .$$

This is the usual result that is normally obtained from perturbation theory applied to the Hamiltonian. It may be used, for example, to calculate the electronic density of states in a liquid metal [30].

§3.4 Binary Alloy - Static Effects

From expression (2.18), we may write the scattering function for a binary substitutional alloy, with c as the concentration of species 2, as

$$(3.12)\quad \Gamma(\underset{\sim}{k},\underset{\sim}{k}',\omega) = |\bar{W}(\underset{\sim}{k},\underset{\sim}{k}')|^2 \, S_{NN}(\underset{\sim}{q},\omega) + c(1-c)\,|W_1(\underset{\sim}{k},\underset{\sim}{k}') - W_2(\underset{\sim}{k},\underset{\sim}{k}')|^2 \, S_I(\underset{\sim}{q},\omega) \, .$$

The first term is the "virtual crystal" contribution to the scattering, and its behaviour will be much the same as that of a pure substance with an average potential $\bar{W}$ associated with each site.

The second term represents the scattering due to deviations from the mean potential. It is a sum of self-correlation terms, one for each ion, and thus displays no "coherence" effects. The static part of $S_I(\underset{\sim}{q},\omega)$ will often dominate the contribution from this term, as may be seen from the following considerations. If we consider a binary alloy in which the two types of ions differ only in their respective potentials, then in the one-phonon approximation, we obtain from (2.19) and (3.3)

$$S_I(\underset{\sim}{q},\omega) = \delta(\omega) + \sum_s \frac{\hbar\,(\underset{\sim}{q}\cdot\hat{\underset{\sim}{e}}_s)^2}{2NM\omega_s}\{(\bar{n}_s+1)\,\delta(\omega-\omega_s) + \bar{n}_s\,\delta(\omega+\omega_s) - (2\bar{n}_s+1)\,\delta(\omega)\}.$$

Using this, we obtain, after some rearrangement

$$\int \frac{S_I(\underset{\sim}{q},\omega)\,d\omega}{(\omega_{\underset{\sim}{k},\underset{\sim}{k}'}-\omega)} = \frac{1}{\hbar\omega_{\underset{\sim}{k},\underset{\sim}{k}'}}\left(1 - \sum_s \frac{\hbar(\underset{\sim}{q}\cdot\hat{e}_s)^2}{2NM\omega_s}\left(\frac{\omega_s(\bar{n}_s+1)}{\omega_s-\omega_{\underset{\sim}{k},\underset{\sim}{k}'}} + \frac{\omega_s\bar{n}_s}{\omega_s+\omega_{\underset{\sim}{k},\underset{\sim}{k}'}}\right)\right).$$

The term involving the phonons may be estimated by using an isotropic Debye model, and at low temperatures, its maximum value will be of the order of

$$\frac{3}{2}\left(\frac{q}{k_F}\right)^2\left(\frac{m}{M}\right)\left(\frac{E_F}{\hbar\omega_D}\right) \approx 4\left(\frac{m}{M}\right)^{\frac{1}{2}} \quad \text{for } q = 2k_F \ .$$

In those cases where this estimate is reasonable, we may replace $S_I(\underset{\sim}{q},\omega)$ in (3.12) by $\delta(\omega)$, and thus obtain for the free energy correction due to this term

$$\phi_2^{(I)} = \frac{2}{N}\sum_{\underset{\sim}{k},\underset{\sim}{k}'}{}' f_{\underset{\sim}{k}}(1-f_{\underset{\sim}{k}'})\frac{c(1-c)|W_1-W_2|^2}{\hbar\omega_{\underset{\sim}{k},\underset{\sim}{k}'}}$$

$$= \frac{2c(1-c)}{N}\sum_{\underset{\sim}{k},\underset{\sim}{k}'}{}' \frac{|W_1(\underset{\sim}{k},\underset{\sim}{k}') - W_2(\underset{\sim}{k},\underset{\sim}{k}')|^2 f_{\underset{\sim}{k}}}{E_{\underset{\sim}{k}} - E_{\underset{\sim}{k}'}} \ .$$

Then, using the same procedure as was used to obtain (3.11), we find the correction to the electron specific heat arising from this term to be

$$(3.13) \qquad (\Delta C_V^{(I)}/C_V^e) = -c(1-c)G_I'(\mu_o)$$

$$G_I(E_{\underset{\sim}{k}}) = \frac{1}{N}\mathcal{P}\int\frac{d\Omega_{\underset{\sim}{k}}}{4\pi}\int\frac{d\Omega_{\underset{\sim}{k}'}}{4\pi}\int_0^\infty dE_{\underset{\sim}{k}'}\,\frac{n_o(E_{\underset{\sim}{k}'})|W_1-W_2|^2}{E_{\underset{\sim}{k}}-E_{\underset{\sim}{k}'}}$$

This result was obtained by Stern in 1966 [16], for the case of a binary substitutional alloy, in which the ions were fixed at sites on a perfect lattice.

Stern applied this result to the case of Ag-Au alloys in an attempt to account for the deviation of the electronic specific heat from linear interpolation, in concentration, between the values for pure Ag and pure Au. Subsequent measurements of the low temperature specific heat by Davis and Rayne [31] indicated that while the concentration dependence of this result is essentially correct, its size (as estimated by Stern) is too small, by about a factor of three.

The reason for this lack of agreement is to be found in the neglect of the ion dynamics. While it is true that the term involving $S_I(\underset{\sim}{q},\omega)$ in (3.12) may be adequately treated in the static approximation, as we have roughly indicated, this does not mean that one may treat all aspects of the electron-ion interaction in this way. At low temperatures, in fact, the dynamic effects, usually referred to in terms of the electron-phonon interaction, are commonly known to be quite important, and we shall return to this point after obtaining some necessary formulae in the following sections. In particular, we shall perform some numerical calculations for the Ag-Au system, in order to indicate the importance of the electron-phonon effects in this case.

§3.5 Low Temperature Specific Heat

In this section we shall derive an approximate expression for the correction to the low temperature electronic specific heat coefficient "γ" due to the term involving $S_{NN}(\underset{\sim}{q},\omega)$. The unperturbed value γ_o is taken to be the free electron value in the case of a disordered system, or the zero-order band structure value in those cases where this concept has meaning. In either case, the S_{NN} term represents scattering of electrons around the Fermi surface due to the emission and absorption of lattice vibrational quanta, and the fact that the Fermi energy is much larger than the energy of the vibrational quanta is an essential point in the derivation.

In addition to this, we will use the fact that the low temperature specific heat is proportional to the density of states, and use the approximation

$$\frac{\Delta\gamma}{\gamma_o} = \frac{\Delta n(E_F)}{n_o(E_F)} \simeq - \left[\frac{\partial}{\partial E_k^{(o)}} \Delta E(\underset{\sim}{k})\right]_{E_{\underset{\sim}{k}}^{(o)}=E_F}$$

where Δ indicates the change in each quantity from the unperturbed value. $\Delta E(\underset{\sim}{k})$ will be obtained by noting that at T = 0 the free energy is equal to the total energy, and using Landau's "quasi-particle" prescription for the energy in a state $\underset{\sim}{k}$:

$$E(\underset{\sim}{k}) \approx \frac{\partial E}{\partial f_{\underset{\sim}{k}}} = \frac{\partial \phi}{\partial f_{\underset{\sim}{k}}} \quad \text{at} \quad T = 0 \ .$$

Part of the development will follow a procedure used successfully by Ashcroft and Wilkins [13,15] in an examination of the electron-phonon enhancement of the specific heat in pure simple metals.

For the free energy correction due to $S_{NN}(\underset{\sim}{q},\omega)$, we have

$$\phi_2^{NN} = \frac{2}{N} \sum_{\underset{\sim}{k},\underset{\sim}{k}'}{}' f_{\underset{\sim}{k}}(1-f_{\underset{\sim}{k}'}) |\bar{W}(\underset{\sim}{k},\underset{\sim}{k}')|^2 \int \frac{d\omega \ S_{NN}(\underset{\sim}{q},\omega)}{\hbar(\omega_{\underset{\sim}{k}\underset{\sim}{k}'} - \omega)}$$

and we thus obtain directly, omitting the superscript on $E_{\underset{\sim}{k}}^{(o)}$ for convenience, and taking account of the two spin states,

$$\frac{\partial \phi_2^{NN}}{\partial f_k} = \frac{1}{N} \sum_{\underset{\sim}{k}' \neq \underset{\sim}{k}} |\bar{W}(\underset{\sim}{k},\underset{\sim}{k}')|^2 \ d\omega \ S_{NN}(\underset{\sim}{q},\omega) \left(\frac{1 - f_{\underset{\sim}{k}'}}{E_{\underset{\sim}{k}} - E_{\underset{\sim}{k}'} - \hbar\omega} - \frac{f_{\underset{\sim}{k}'}}{E_{\underset{\sim}{k}} - E_{\underset{\sim}{k}'} + \hbar\omega} \right)$$

$$= \frac{1}{N} \sum_{\underset{\sim}{k}' \neq \underset{\sim}{k}} |\bar{W}(\underset{\sim}{k},\underset{\sim}{k}')|^2 \ d\omega \ S_{NN}(\underset{\sim}{q},\omega) \left(\frac{\theta(E_{\underset{\sim}{k}'} - E_F)}{E_{\underset{\sim}{k}} - E_{\underset{\sim}{k}'} - \hbar\omega} - \frac{\theta(E_F - E_{\underset{\sim}{k}'})}{E_{\underset{\sim}{k}} - E_{\underset{\sim}{k}'} + \hbar\omega} \right)$$

where $\theta(E_F - E_{\underset{\sim}{k}'})$ is the Fermi function at $T = 0$,

$$\theta(E_F - E_{\underset{\sim}{k}'}) = \begin{cases} 1 & \text{if} \quad E_{\underset{\sim}{k}'} < E_F \\ 0 & \text{if} \quad E_{\underset{\sim}{k}'} > E_F \end{cases} \ .$$

Changing the sum over $\underset{\sim}{k}'$ to an integral, we have

$$\frac{\partial \phi_2^{NN}}{\partial f_{\underset{\sim}{k}}} = \frac{1}{N}\int_0^{\infty} d\underset{\sim}{E}_{\underset{\sim}{k}'} n_o(\underset{\sim}{E}_{\underset{\sim}{k}'}) \int \frac{d\underset{\sim}{\Omega}_{\underset{\sim}{k}'}}{4\pi} |\bar{W}(\underset{\sim}{k},\underset{\sim}{k}')|^2 \int d\omega\ S_{NN}(\underset{\sim}{q},\omega) \cdot$$

$$\left[\frac{\theta(\underset{\sim}{E}_{\underset{\sim}{k}'} - E_F)}{\underset{\sim}{E}_{\underset{\sim}{k}} - \underset{\sim}{E}_{\underset{\sim}{k}'} - \hbar\omega} + \frac{\theta(E_F - \underset{\sim}{E}_{\underset{\sim}{k}'})}{\underset{\sim}{E}_{\underset{\sim}{k}} - \underset{\sim}{E}_{\underset{\sim}{k}'} + \hbar\omega}\right]$$

$$= \frac{1}{N}\int_{-E_F}^{\infty} d\underset{\sim}{\varepsilon}_{\underset{\sim}{k}'} n_o(E_F + \underset{\sim}{\varepsilon}_{\underset{\sim}{k}'}) \int \frac{d\underset{\sim}{\Omega}_{\underset{\sim}{k}'}}{4\pi} |\bar{W}(\underset{\sim}{k},\underset{\sim}{k}')|^2 \int d\omega\ S_{NN}(\underset{\sim}{q},\omega) \cdot$$

$$\left[\frac{\theta(\underset{\sim}{\varepsilon}_{\underset{\sim}{k}'})}{\underset{\sim}{\varepsilon}_{\underset{\sim}{k}} - \underset{\sim}{\varepsilon}_{\underset{\sim}{k}'} - \hbar\omega} + \frac{\theta(-\underset{\sim}{\varepsilon}_{\underset{\sim}{k}'})}{\underset{\sim}{\varepsilon}_{\underset{\sim}{k}} - \underset{\sim}{\varepsilon}_{\underset{\sim}{k}'} + \hbar\omega}\right]$$

where $\underset{\sim}{\varepsilon}_{\underset{\sim}{k}'} = (\underset{\sim}{E}_{\underset{\sim}{k}'} - E_F)$. Using the θ-functions to define the limits of integration explicitly, and treating the first and second terms separately we obtain

$$\frac{\partial \phi_2^{NN}}{\partial f_{\underset{\sim}{k}}} = \frac{1}{N}\int_0^{\infty} d\underset{\sim}{\varepsilon}_{\underset{\sim}{k}'} n_o(E_F + \underset{\sim}{\varepsilon}_{\underset{\sim}{k}'}) \int \frac{d\underset{\sim}{\Omega}_{\underset{\sim}{k}'}}{4\pi} |\bar{W}(\underset{\sim}{k},\underset{\sim}{k}')|^2 \int \frac{d\omega\ S_{NN}(\underset{\sim}{q},\omega)}{\underset{\sim}{\varepsilon}_{\underset{\sim}{k}} - \underset{\sim}{\varepsilon}_{\underset{\sim}{k}'} - \hbar\omega}$$

$$+ \frac{1}{N}\int_0^{E_F} d\underset{\sim}{\varepsilon}_{\underset{\sim}{k}'} n_o(E_F - \underset{\sim}{\varepsilon}_{\underset{\sim}{k}'}) \int \frac{d\underset{\sim}{\Omega}_{\underset{\sim}{k}'}}{4\pi} |\bar{W}(\underset{\sim}{k},\underset{\sim}{k}')|^2 \int \frac{d\omega\ S_{NN}(\underset{\sim}{q},\omega)}{\underset{\sim}{\varepsilon}_{\underset{\sim}{k}} + \underset{\sim}{\varepsilon}_{\underset{\sim}{k}'} + \hbar\omega}$$

$$\approx \frac{n_o(E_F)}{N}\int_0^{\infty} d\underset{\sim}{\varepsilon}_{\underset{\sim}{k}'} \int \frac{d\underset{\sim}{\Omega}_{\underset{\sim}{k}'}}{4\pi} |\bar{W}(\underset{\sim}{k},\underset{\sim}{k}')|^2 \int d\omega\ S_{NN}(\underset{\sim}{q},\omega) \left[\frac{1}{\underset{\sim}{\varepsilon}_{\underset{\sim}{k}} - \underset{\sim}{\varepsilon}_{\underset{\sim}{k}'} - \hbar\omega}\right.$$

$$\left. + \frac{1}{\underset{\sim}{\varepsilon}_{\underset{\sim}{k}} + \underset{\sim}{\varepsilon}_{\underset{\sim}{k}'} + \hbar\omega}\right]$$

where it has been assumed that E_F is much greater than those values of $\varepsilon_{\underset{\sim}{k}'}$ for which the integrand is appreciably different from zero, and that the zero-order density of states does not vary greatly over this interval.

From this expression we then obtain,

$$\left(\frac{\Delta\gamma}{\gamma_o}\right)^{NN} = \left[-\frac{\partial}{\partial E_{\underset{\sim}{k}}}\frac{\partial\phi_2^{NN}}{\partial f_{\underset{\sim}{k}}}\right]_{E_{\underset{\sim}{k}}=E_F} = \left[-\frac{\partial}{\partial \varepsilon_{\underset{\sim}{k}}}\frac{\partial\phi_2^{NN}}{\partial f_{\underset{\sim}{k}}}\right]_{\varepsilon_{\underset{\sim}{k}}=0}$$

$$\approx \frac{n_o(E_F)}{N}\int_0^\infty d\varepsilon_{\underset{\sim}{k}'}\int\frac{d\Omega_{\underset{\sim}{k}'}}{4\pi}|\bar{W}(\underset{\sim}{k},\underset{\sim}{k}')|^2\int d\omega S_{NN}(\underset{\sim}{q},\omega)\cdot$$

$$\left[-\frac{\partial}{\partial\varepsilon_{\underset{\sim}{k}}}\left(\frac{1}{\varepsilon_{\underset{\sim}{k}}-\varepsilon_{\underset{\sim}{k}'}-\hbar\omega}+\frac{1}{\varepsilon_{\underset{\sim}{k}}-\varepsilon_{\underset{\sim}{k}'}+\hbar\omega}\right)\right]_{\varepsilon_{\underset{\sim}{k}}=0}$$

$$= \frac{n_o(E_F)}{N}\int\frac{d\Omega_{\underset{\sim}{k}'}}{4\pi}|\bar{W}(\underset{\sim}{k},\underset{\sim}{k}')|^2\int d\omega\ S_{NN}(\underset{\sim}{q},\omega)\int_0^\infty d\varepsilon_{\underset{\sim}{k}'}\ \frac{\partial}{\partial\varepsilon_{\underset{\sim}{k}'}}\left(\frac{-2}{\varepsilon_{\underset{\sim}{k}'}+\hbar\omega}\right)$$

$$= \frac{2n_o(E_F)}{N}\int\frac{d\Omega_{\underset{\sim}{k}'}}{4\pi}|\bar{W}(\underset{\sim}{k},\underset{\sim}{k}')|^2\int d\omega\ \frac{S_{NN}(\underset{\sim}{q},\omega)}{\hbar\omega}$$

where we have neglected any explicit energy dependence of the pseudopotentials. Consistent with this, we will treat the pseudopotentials in the local or "on-Fermi sphere" approximation in the rest of this development, so that they may be written as a function of $\underset{\sim}{q} = \underset{\sim}{k}-\underset{\sim}{k}'$ only. Then, introducing the function,

$$F(\underset{\sim}{q}) = \frac{2n_o(E_F)}{N}|\bar{W}(\underset{\sim}{q})|^2\int d\omega\ \frac{S_{NN}(\underset{\sim}{q},\omega)}{\hbar\omega}$$

we are led to the following results:

$$(3.14)\qquad \left(\frac{\Delta\gamma}{\gamma_o}\right)^{NN} = \int\frac{d\Omega_{k'}}{4\pi}\ F(\underset{\sim}{k}-\underset{\sim}{k}')$$

$$\rightarrow \int\frac{d\Omega_k}{4\pi}\int\frac{d\Omega_{k'}}{4\pi}\ F(\underset{\sim}{k}-\underset{\sim}{k}')$$

$$\rightarrow \frac{1}{k_F^4}\int dk\ k^2\delta(k-k_F)\int dk'k'^2\delta(k'-k_F)\int\frac{d\Omega_k}{4\pi}\int\frac{d\Omega_{k'}}{4\pi}\ F(\underset{\sim}{k}-\underset{\sim}{k}')$$

$$= \frac{1}{(4\pi k_F^2)^2}\int d^3k\int d^3k'\,F(\underset{\sim}{k}-\underset{\sim}{k}')\,\delta(k-k_F)\,\delta(k'-k_F)$$

$$= \frac{1}{(4\pi k_F^2)^2}\int_{q<2k_F} d^3k\int d^3k\ F(\underset{\sim}{q})\,\delta(k-k_F)\,\delta(|\underset{\sim}{k}-\underset{\sim}{q}|-k_F)\quad .$$

The integral of the delta-functions over d^3k may be evaluated directly as

$$\int_0^{2\pi} d\phi\int_{-1}^{+1} du\int_0^{\infty} dk\ k^2\delta(k-k_F)\,\delta((k^2+q^2-2kqu)^{\frac{1}{2}}-k_F)$$

$$= 2\pi k_F^2\int_{-1}^{+1} du\ \delta((k_F^2+q^2-2k_Fqu)^{\frac{1}{2}}-k_F)$$

$$= \frac{2\pi k_F}{q}\int_{|k_F-q|}^{|k_F+q|} dx\ x\ \delta(x-k_F)$$

$$= \frac{2\pi k_F^2}{q}\quad .$$

Using this result in (3.14), separating the angular variables, and defining a function

$$(3.15)\quad F_{AV}(q) = \int \frac{d\Omega_q}{4\pi} F(\underset{\sim}{q}) = \frac{2n_o(E_F)}{N} \int \frac{d\Omega_q}{4\pi} |\bar{W}(\underset{\sim}{q})|^2 \int d\omega \, \frac{S_{NN}(\underset{\sim}{q},\omega)}{\hbar\omega}$$

we obtain the final result

$$(3.16)\quad \left(\frac{\Delta\gamma}{\gamma_o}\right)^{NN} = \frac{1}{2k_F^2} \int_0^{2k_F} dq \; q \; F_{AV}(q) \quad .$$

The form of this result is seen to be quite similar to the variational expression for the resistivity of the type of substances which we are considering here [21]. The differences are that in the resistivity formula there is an extra factor q^2 in the integrand, and $F(\underset{\sim}{q})$ is replaced by a function proportional to $I(\underset{\sim}{q})$ given by (3.7).

Indeed, in the present case, one may replace $|\bar{W}(\underset{\sim}{q})|^2 S_{NN}(\underset{\sim}{q},\omega)$ by the full scattering function $\Gamma(\underset{\sim}{q},\omega)$ as long as any "static" contributions, involving $\delta(\omega)$, are treated separately, such as in the preceding section.

CHAPTER 4

NUMERICAL CALCULATIONS

4.1 Electron-Phonon Enhancement for Na

In the one-phonon approximation, we may use (3.4) to obtain for a pure substance at T = 0:

$$(4.1)\qquad \int d\omega \frac{S(\underset{\sim}{q},\omega)}{\hbar\omega} = \sum_{s} \frac{(\underset{\sim}{q}\cdot\hat{e}_{s})^{2}}{2M\omega_{s}^{2}} \delta_{\underset{\sim}{q}-\underset{\sim}{Q},\underset{\sim}{G}}$$

$$= \sum_{\underset{\sim}{G},\xi} \frac{(\underset{\sim}{q}\cdot\hat{e}_{\underset{\sim}{q}-\underset{\sim}{G},\xi})^{2}}{2M\omega^{2}_{\underset{\sim}{q}-\underset{\sim}{G},\xi}} .$$

On the other hand, if we calculate the structure factor $S(\underset{\sim}{q}) = I(\underset{\sim}{q})/|W(\underset{\sim}{q})|^{2}$ appearing in the resistivity formula, we have

$$S(\underset{\sim}{q}) = \int d\omega \frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} S(\underset{\sim}{q},\omega)$$

$$= 2\beta\hbar \sum_{\underset{\sim}{G},s} \frac{\hbar(\underset{\sim}{q}\cdot\hat{e}_{s})^{2}}{2M} \frac{\delta_{\underset{\sim}{q}-\underset{\sim}{Q},\underset{\sim}{G}}}{(e^{\beta\hbar\omega_{s}} - 1)(1 - e^{-\beta\hbar\omega_{s}})} .$$

At high temperatures this reduces to

$$S(\underset{\sim}{q}) = 2k_{B}T \sum_{\underset{\sim}{G},\xi} \frac{(\underset{\sim}{q}\cdot\hat{e}_{\underset{\sim}{q}-\underset{\sim}{G},\xi})^{2}}{2M\omega^{2}_{\underset{\sim}{q}-\underset{\sim}{G},\xi}}$$

which, apart from the factor $2k_BT$, is identical with expression (4.1), recognizing of course, that the phonon frequencies are slightly different in the two cases.

Ignoring this difference for present purposes, we see that $F_{AV}(q)$ is proportional to the angular averaged structure factor $S_{AV}(q)$:

$$F_{AV}(q) \propto S_{AV}(q) = \int \frac{d\Omega_{\underline{q}}}{4\pi} \; S(\underline{q}) \quad .$$

Greene and Kohn [32] have calculated this function for Na and found that it was small and essentially constant for low q-values (normal processes) and rose steeply as one approached $q = 2k_F$ (umklapp processes). This behaviour is not peculiar to Na of course, and is a characteristic feature of the structure factors. In general, one will find sharp peaks in $S(\underline{q})$ whenever $\underline{q}$ is close to a reciprocal lattice vector, the shortest of which lies just above $2k_F$ for the monovalent metals, and just below $2k_F$ for the polyvalent metals.

Another feature of the results of [32] is that at high and low temperatures alike (273°K and 40°K), the ratio of the structure factor at $q = 2k_F$ to that at $q = 0$ is unchanged, and in both cases is found to be:

$$\frac{S_{AV}(2k_F)}{S_{AV}(0)} = 40 \quad .$$

We may readily obtain a qualitative understanding of these effects by considering the case when $\underset{\sim}{q}$ is parallel to one of the reciprocal lattice vectors $\underset{\sim}{G}$. If we ignore dispersion, the value of (4.1) in this direction is given by

$$(4.2) \qquad \frac{1}{2Ms_G^2}\left\{\theta\left(\frac{G}{2} - q\right) + \theta\left(q - \frac{G}{2}\right)\frac{q^2}{(q-G)^2}\right\}$$

where s_G is the velocity of a longitudinal wave in the direction of $\underset{\sim}{G}$, and θ is the unit step function. The function in curly brackets is equal to unity up to the zone boundary ($q = G/2$), and thereafter rises steeply as q approaches G. For Na (B.C.C. structure) the shortest $\underset{\sim}{G}$ is the (110) direction, and the ratio of (4.2) evaluated at $q = 2k_F$ to the value at $q = 0$ is given by

$$\left(\frac{2k_F}{2k_F - G_{110}}\right)^2 = 50$$

with $G_{110}/2k_F = 1.141$. This result is the same at all temperatures, since k_F and G are both proportional to the inverse of the lattice constant.

In order to do a simple calculation of the electron-phonon (e.p.) enhancement factor for Na, we

will use the functional form given by (4.2) in place of the averaged structure factor, modified to the extent that we will define an effective $G \equiv \tilde{G}$, such that

$$\left(\frac{2k_F}{2k_F - \tilde{G}}\right)^2 = 40$$

which gives $\tilde{G}/2k_F = 1.158$. The behaviour of (4.2) for this value of $\tilde{G}$ is illustrated in Fig. 1. It differs from the correct form of the structure factor in that the latter is a little higher in the intermediate ($q \sim k_F$) region, this difference being mainly due to our neglect of dispersion. For polyvalent metals, of course, our approximation for S_{AV} may not be used, because of the divergence at $q = G$, and one must do a more careful calculation in these cases. See, for example, the resistivity calculations of Dynes and Carbotte [33].

Using (4.2) in (3.15) and (3.16) thus gives

$$(4.3) \qquad \left(\frac{\Delta\gamma}{\gamma_o}\right)_{e.p.} = \frac{2n_o(E_F)}{NE_F}\left(\frac{E_F}{Ms^2}\right)\left[\int_0^{a/2} dx\, x|W(x)|^2 + \int_{a/2}^{1} dx \frac{x^3}{(x-a)^2}|W(x)|^2\right]$$

where $a = \tilde{G}/2k_F$, $x = q/2k_F$ and $n_o(E_F) = 3N/2E_F$.

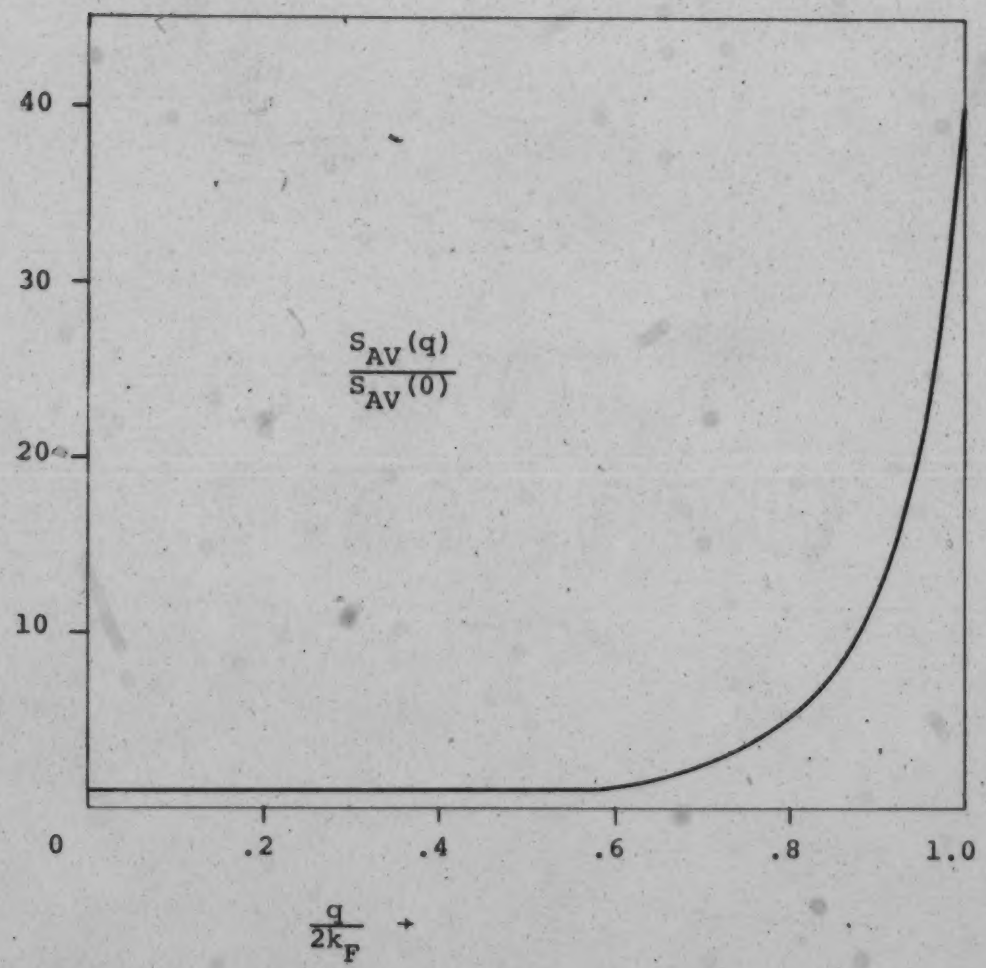

Fig. 1. Approximate structure factor for Na.
See equation 4.2.

A value for E_F/Ms^2 is obtained by calculating this quantity for longitudinal waves in the (100), (110) and (111) directions, and averaging the results. This gives a value for Na of $E_F/Ms^2 = 1.22$.

For a pseudopotential, we will use the simple functional form suggested by Veljković and Slavić [34], namely

$$(4.4) \qquad W(x) = -\frac{2}{3} E_F \left(\frac{\sin bx}{bx}\right)$$

which they fitted to the Heine-Abarenkov form factors [35,36] for a number of simple metals. In real space, this corresponds to a pseudopotential of the form:

$$V(r) = -\left(\frac{2}{3} E_F\right) \frac{V/N}{4\pi r_o^2} \delta(r-r_o)$$

defining a "pseudo-atom" of radius $r_o = b/2k_F$, which turns out to be a little smaller than the atomic radius. For Na, these authors give a value $b = 2\pi(.56121)$, and we obtain, upon performing the integrations in (4.3):

$$\left(\frac{\Delta\gamma}{\gamma_o}\right)_{\text{e.p.}} = .20 \qquad \text{(Na)}$$

with 30% of this value coming from the umklapp processes.

This result compares well with the value .18 given by Ashcroft and Wilkins [13], and if we add the

electron-electron contribution of .06 quoted by these authors, we arrive at

$$\left(\frac{\gamma}{\gamma_o}\right) = 1.26 \qquad \text{(Na)}$$

compared with the experimental value 1.25 quoted in [13].

§4.2 Binary Alloys - Interference and Impurity Contributions

To return to the binary substitutional alloy, we write the scattering function, with local pseudopotentials, and treating the S_{CC} part in the "static" approximation, as:

$$\Gamma(\underset{\sim}{q},\omega) = |\bar{W}(q)|^2 \, S_{NN}(\underset{\sim}{q},\omega) + c(1-c)\,|\Delta W(q)|^2 \delta(\omega)$$

where $\Delta W(q) = W_1(q) - W_2(q)$. We may note that since $\bar{W} = (1-c)W_1 + cW_2$, we have

$$\bar{W}^2 = (1-c)^2 W_1^2 + c^2 W_2^2 + 2c(1-c)W_1 W_2$$

$$= (1-c)W_1^2 + cW_2^2 - c(1-c)(\Delta W)^2$$

and thus $\Gamma(\underset{\sim}{q},\omega)$ may be written as

$$(4.5) \quad \Gamma(\underset{\sim}{q},\omega) = (1-c)\,|W_1|^2 S_{NN}(\underset{\sim}{q},\omega) + c\,|W_2|^2 S_{NN}(\underset{\sim}{q},\omega)$$

$$- c(1-c)\,|\Delta W|^2 S_{NN}(\underset{\sim}{q},\omega) + c(1-c)\,|\Delta W|^2 \delta(\omega) \; .$$

When we use this expression to calculate corrections to the electronic specific heat coefficient, we will have four contributions. The first two terms will give the linear interpolation between the electron-ion enhancement factors for the pure substances, while the third and fourth terms represent quadratic deviations due to dynamic and static effects respectively. It is interesting to note that the last two terms in (4.5) have the same concentration dependence, and involve the same combination of pseudopotentials. A similar result is also true for ν-component alloys.

The contributions to the specific heat coefficient due to the non-linear terms may be written, using (3.16) and (3.13), as

$$\left(\frac{\Delta\gamma}{\gamma_o}\right)_{\text{int}} = -c(1-c)\,\frac{n_o(E_F)}{Nk_F^2}\int_0^{2k_F} dq\; q\,|\Delta W(q)|^2 \int\frac{d\Omega_q}{4\pi}\int d\omega\;\frac{S_{NN}(\underset{\sim}{q},\omega)}{\hbar\omega}$$

$$\left(\frac{\Delta\gamma}{\gamma_o}\right)_{\text{imp}} = c(1-c)\,\frac{n_o(E_F)}{Nk_F^2}\,\frac{(2\pi)^3}{4\pi V}\,\frac{d}{dk}\left(\mathcal{P}\sum_{\underset{\sim}{q}\neq 0}\frac{|\Delta W(\underset{\sim}{q})|^2}{E_{\underset{\sim}{k}-\underset{\sim}{q}} - E_{\underset{\sim}{k}}}\right)_{k=k_F}$$

where int = "interference", imp = "impurity", and we have taken $E_k = \hbar^2k^2/2m$.

In order to investigate the qualitative behaviour and relative importance of these two terms, we will again use (4.2) as an approximation to the structure factor, and thus obtain, after some direct algebra:

$$\left(\frac{\Delta\gamma}{\gamma_o}\right)_{int} = \left[c(1-c)\,\frac{2n_o(E_F)}{NE_F}\right] f_{int}$$

$$\left(\frac{\Delta\gamma}{\gamma_o}\right)_{imp} = \left[c(1-c)\,\frac{2n_o(E_F)}{NE_F}\right] f_{imp}$$

where we have defined:

$$(4.6)\qquad f_{int} = -\left(\frac{E_F}{Ms^2}\right)\left(\int_0^{a/2} dx\; x|\Delta W(x)|^2 + \int_{a/2}^{1} dx\; \frac{x^3}{(x-a)^2}|\Delta W(x)|^2\right)$$

$$(4.7)\qquad f_{imp} = \mathcal{P}\int_0^{\infty} dx\left(\frac{2x^2}{x^2-1}\right)\left(\frac{1}{2} - \frac{x^2-1}{4x}\,\ell n\left|\frac{x+1}{x-1}\right|\right)|\Delta W(x)|^2 \quad .$$

It is interesting to note that the factor involving the logarithms is the well known screening function for the electron gas. E_F/Ms^2 in this context is to be viewed as an averaged of the pure metal values.

The interference term is always negative, and thus constitutes a reduction of the electron-phonon enhancement upon alloying. The impurity term may be of either sign, and for $|\Delta W(x)|$ = constant, it is zero. It will be positive if the integrand (apart from the factor $1/(x^2-1)$) is greater to the right of the singularity, and negative if it is greater to the left of it.

For illustrative purposes, we will examine a series of "theoretical" alloys in which each constituent has a pseudopotential of the form (4.4), thus giving for ΔW:

$$\Delta W(x) = W_1(0)\left(\frac{\sin 2\pi\beta_1 x}{2\pi\beta_1 x}\right) - W_2(0)\left(\frac{\sin 2\pi\beta_2 x}{2\pi\beta_2 x}\right) \quad .$$

For most metals, the published information indicates that the first zero (q_o) of the pseudopotentials occurs between $q = k_F$ and $q = 2k_F$ [7]. For the form which we have chosen, the first zero occurs at

$$\frac{q_o}{k_F} = \frac{1}{\beta} \quad .$$

Thus, if we allow β_1 and β_2 to vary between 0.5 and 1.0, we will cover the range of interest.

We will use the F.C.C. lattice structure, and in each case will calculate f_{int} for two values of "a", namely $a = G_{111}/2k_F$ and $a = G_{200}/2k_F$. These are the two shortest vectors for this lattice, and should represent upper and lower bounds for f_{int}.

Case 1 : $\beta_1 = \beta_2$

As a first example, we shall consider the case in which q_o is the same for both constituents, so that

$$|\Delta W(x)|^2 = |\Delta W(0)|^2 \left(\frac{\sin 2\pi\beta x}{2\pi\beta x}\right)^2 \quad .$$

In this case, both f_{int} and f_{imp} are negative for all values of β, and the results of the computations are given in Fig. 2, with $E_F/Ms^2 = 1$.

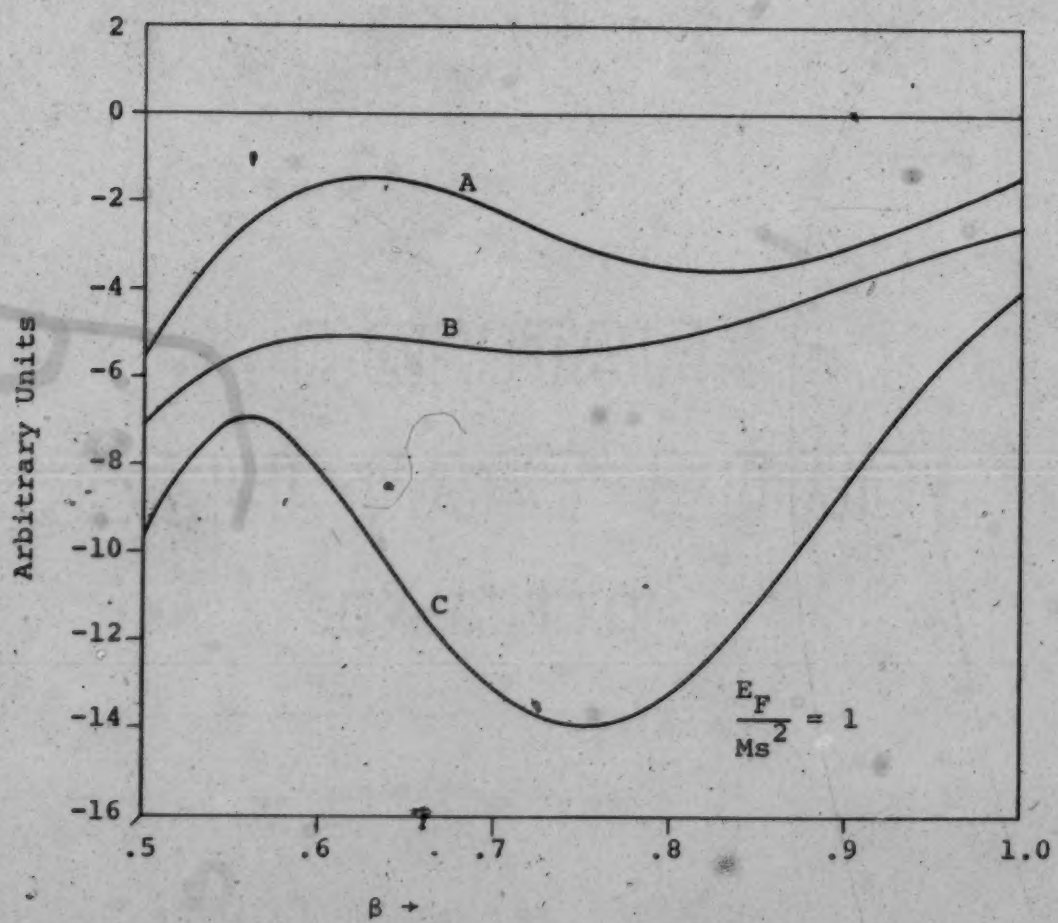

Fig. 2. Interference and impurity contributions to alloy specific heat. See §4.2 (case 1) A - f_{imp}, B - f_{int}^{200}, C - f_{int}^{111}.

The "correct" value for the interference term should lie somewhere between $f_{int}^{(111)}$ and $f_{int}^{(200)}$ subject, of course, to scaling, depending on whether E_F/Ms^2 is less than or greater than unity.

In any case, we see that both the impurity and interference terms are of comparable magnitude, a conclusion which will not likely be altered, in substance, for real materials.

Case 2 : $W_1(0) = W_2(0)$

In this example, the pseudopotentials for each constituent have the same value at $q = 0$, but have different values of q_o. The impurity contribution takes on both negative and positive values for different combinations of β_1 and β_2, as indicated in Fig. 3.

We see that for a fixed value of β_2 say, f_{imp} tends to negative values if $\beta_1 < \beta_2$ and will thus act in the same direction as f_{int}. For $\beta_1 > \beta_2$, however, the tendency is to positive values for f_{imp}. One might thus expect some cancellation between f_{int} and f_{imp} for these cases, since both functions are again in the same range as far as magnitude is concerned, as one may see from Fig. 4 and Fig. 5. These results are for β_2 fixed at .65 and .85 respectively, with β_1 ranging from 0.5 to 1.0.

$\beta_1 \downarrow$ \ $\beta_2 \rightarrow$	.50	.55	.60	.65	.70	.75	.80	.85	.90	.95	1.00
.50	0	-	-	-	-	-	-	-	-	-	-
.55	-	0	-	-	-	-	-	-	-	-	-
.60	-	-	0	-	-	-	-	-	-	-	+
.65	-	-	-	0	-	-	-	+	+	+	+
.70	-	-	-	-	0	+	+	+	+	+	+
.75	-	-	-	-	+	0	+	+	+	+	+
.80	-	-	-	-	+	+	0	+	+	+	+
.85	-	-	-	+	+	+	+	0	+	+	+
.90	-	-	-	+	+	+	+	+	0	+	+
.95	-	-	-	+	+	+	+	+	+	0	-
1.00	-	-	+	+	+	+	+	+	+	-	0

Fig. 3. Sign of impurity term for various combinations of β_1 and β_2. See §4.2 (case 2).

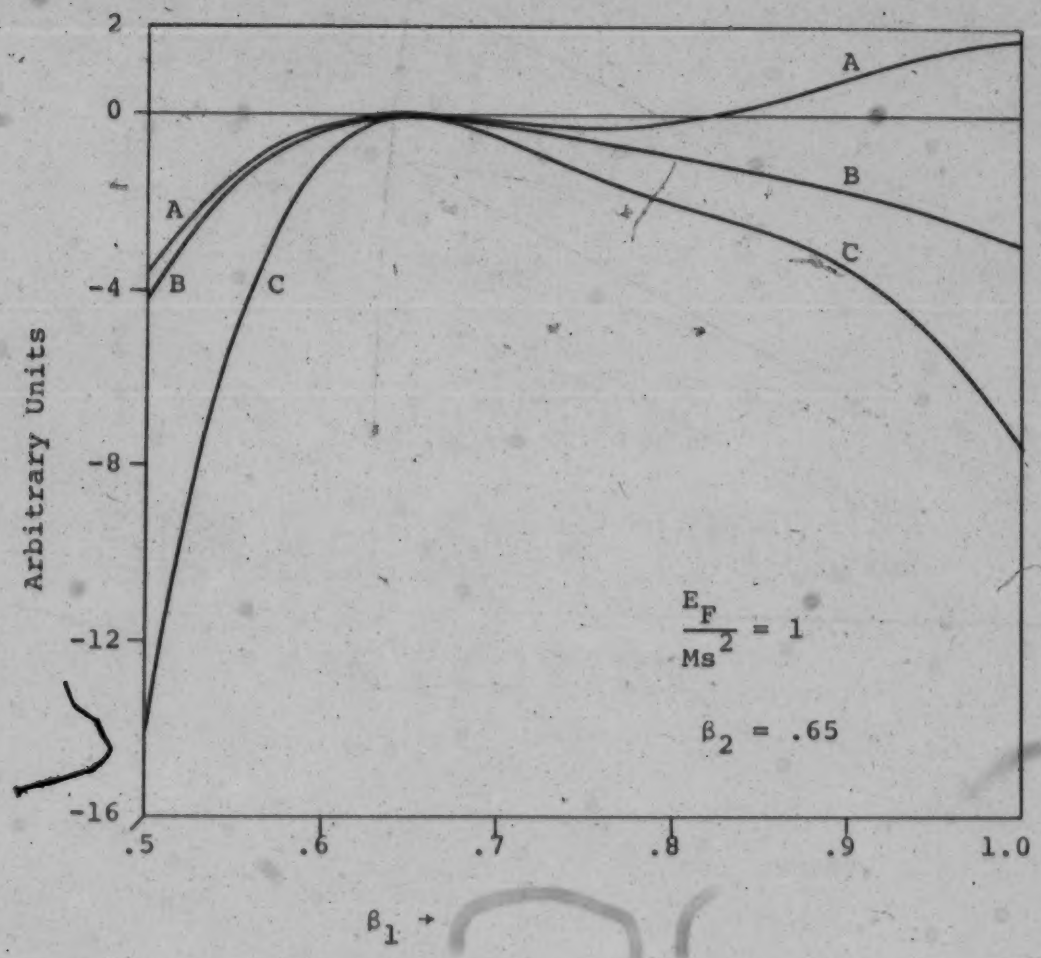

Fig. 4. Interference and impurity contributions to alloy specific heat. See §4.2 (case 2) A - f_{imp}, B - f_{int}^{200}, C - f_{int}^{111}.

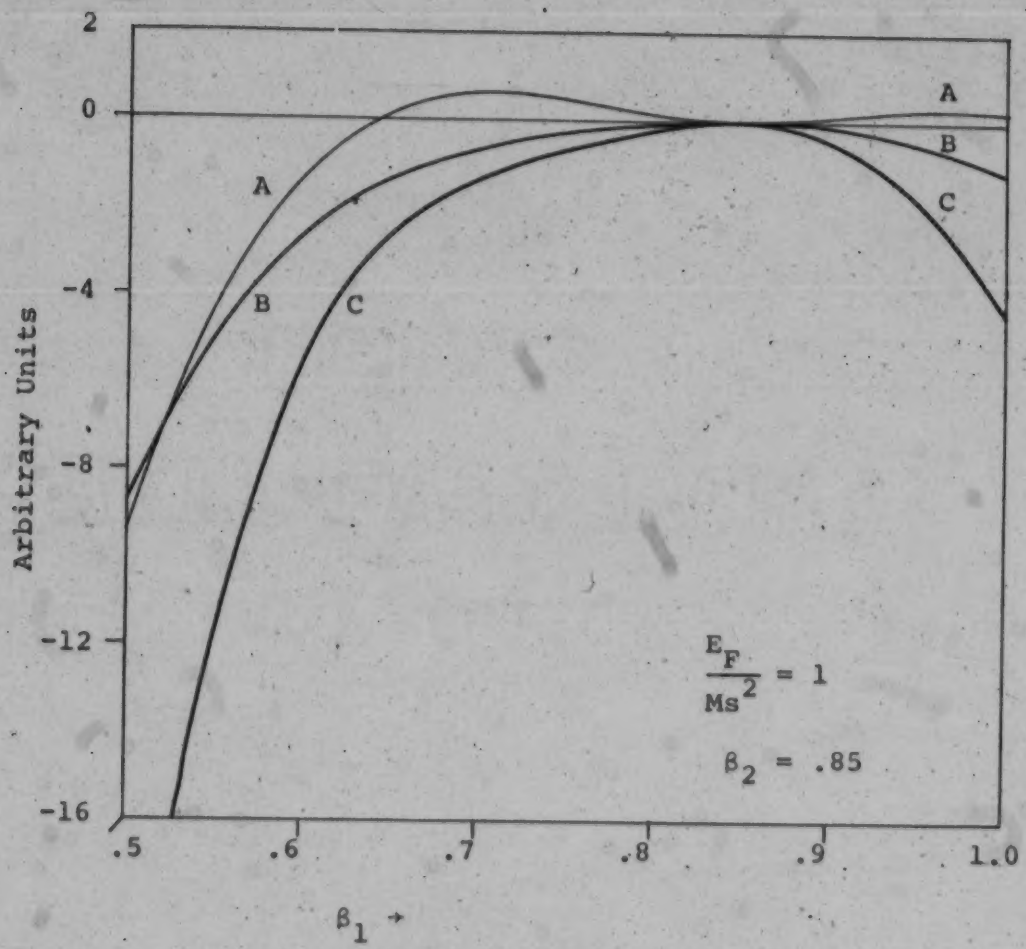

Fig. 5. Interference and impurity contributiond to alloy specific heat. See §4.2 (case 2) F - f_{imp}, B - f_{int}^{200}, C - f_{int}^{111}.

One may also see that f_{int} and f_{imp} tend to assume their largest (absolute) values when β_1 and β_2 are appreciably different from one another. This would be expected intuitively, since different values of these parameters are an indication of different scattering properties for the alloy constituents.

The same trend is followed when $W_1(0)$ and $W_2(0)$ are allowed to vary at the same time as β_1 and β_2, and the qualitative nature of the results are much the same.

§4.3 Ag-Au System - General Considerations

Continuing from (4.5), we may write the electronic specific heat coefficient as:

$$(4.8) \quad \gamma = \gamma_o + (1-c)\Delta\gamma_{ep}^{(1)} + c\Delta\gamma_{ep}^{(2)} + c(1-c)(\Delta\gamma_{int} + \Delta\gamma_{imp})$$

where we have changed notation slightly, in order to write the concentration factors explicitly.

If we now assume that the zero-order coefficient varies no more than linearly between the pure metals, and write it as:

$$(4.9) \quad \gamma_o = (1-c)\gamma_o^{(1)} + c\gamma_o^{(2)}$$

we may see that

$$\frac{\gamma-\gamma_o}{\gamma_o} = \frac{(1-c)\Delta\gamma_{ep}^{(1)}+c\Delta\gamma_{ep}^{(2)}}{(1-c)\gamma_o^{(1)}+c\gamma_o^{(2)}} + \frac{c(1-c)(\Delta\gamma_{int}+\Delta\gamma_{imp})}{(1-c)\gamma_o^{(1)}+c\gamma_o^{(2)}}$$

On the other hand, if we collect all the linear terms in (4.8), we may define:

$$(4.10) \qquad \tilde{\gamma}_o = (1-c)(\gamma_o^{(1)}+\Delta\gamma_{ep}^{(1)}) + c(\gamma_o^{(2)}+\Delta\gamma_{ep}^{(2)})$$

and it is seen that

$$(4.11) \qquad \frac{\gamma-\tilde{\gamma}_o}{\tilde{\gamma}_o} = \frac{c(1-c)(\Delta\gamma_{int}+\Delta\gamma_{imp})}{(1-c)(\gamma_o^{(1)}+\Delta\gamma_{ep}^{(1)}) + c(\gamma_o^{(2)}+\Delta\gamma_{ep}^{(2)})} .$$

For $c = 0$ or 1, $\tilde{\gamma}_o$ is equal to the measured value of the specific heat coefficients for the pure metals (including band structure and electron-phonon deviations from the free electron values), and is the linear interpolation between these values for $c \neq 0$ or 1.

Davis and Rayne [31] fitted their electronic specific heat measurements for Ag-Au alloys to an expression of the form

$$(4.12) \qquad \frac{\gamma-\gamma_o(c)}{\gamma_o(c)} = \kappa\, c(1-c)$$

in which $\gamma_o(c)$ was the linear interpolation between their experimental results for pure Ag and Au. A least squares fit to their data gave a value of $\kappa = -.138$, with the largest deviations being at the Au end of the

alloy series, as one may see from Fig. 6, where we have plotted their results.

These authors assumed $\gamma_o(c)$ to be the zero-order "band structure" coefficient given by (4.9). This was consistent with the model of Stern [16], which they wished to test for concentration dependence, and in which the dynamic contributions are assumed to be zero.

In point of fact, however, since $\gamma_o(c)$ was obtained from the experimental data, it is clear that this function is identical with $\tilde{\gamma}_o$ as defined by (4.10), and already includes the linear electron-phonon enhancement.

Thus, in reality, the function which Davis and Rayne fitted to their data is given by (4.11), and the coefficient "κ" determined by them contains the dynamic effects of the interaction through $\Delta\gamma_{int}$, as well as the static contribution investigated by Stern, and given in our case by $\Delta\gamma_{imp}$. We will consider these effects more explicitly in the following sections.

Note that for cases in which the zero-order coefficient has more than linear variation with concentration, this will simply add another term to the numerator of (4.11), and may be thus readily included in the analysis.

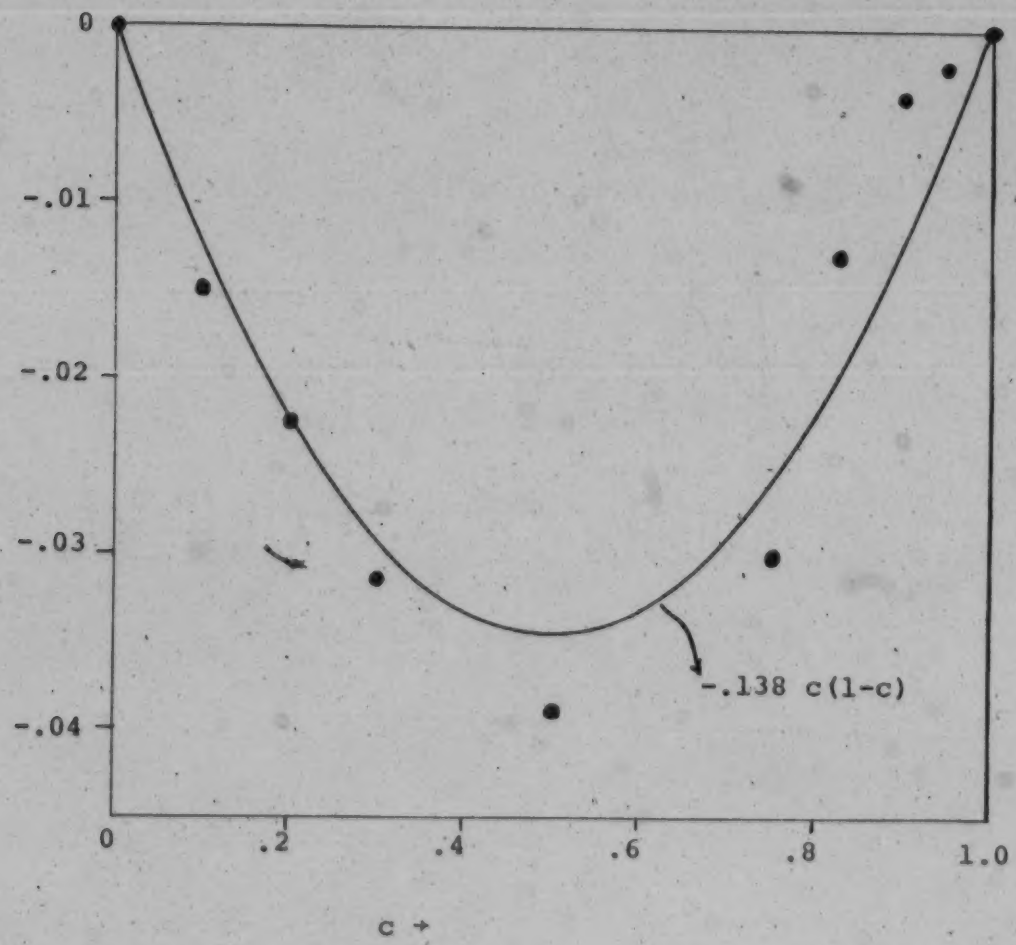

Fig. 6. Deviation from linearity (in concentration) of specific heat coefficient for Ag-Au
Points - Davis and Rayne experimental data.
Solid curve - least squares fit to data.
See equation 4.12.

§4.4 Electron-Phonon Enhancement for Ag and Au

For Ag and Au (F.C.C. structure), the first reciprocal lattice vector (G_{111}) is shorter than the shortest vector (G_{110}) for Na, and one could thus expect the structure factor to be relatively larger in the back-scattering region ($q \sim 2k_F$). We will use the form (4.2) to represent the structure factor, and in the absence of any published information, will choose a value of "a" such that $S_{AV}(2k_F)/S_{AV}(0)$ is 4/5 of the value calculated with the shortest reciprocal lattice vector, as in Na. This gives $a = G/2k_F = 1.123$, and

$$\left(\frac{2k_F}{2k_F - \tilde{G}}\right)^2 = 66 \quad .$$

Then, using expression (4.3), and the pseudopotentials calculated by Moriarty [37] (Fig. 7), we obtain, using $E_F/Ms^2 = 0.34$ and 0.24 for Ag and Au respectively:

$$\left(\frac{\Delta\gamma}{\gamma_o}\right)_{e.p.} = .36 \left(\frac{m_b}{m}\right) \qquad \text{(Ag)}$$

$$\left(\frac{\Delta\gamma}{\gamma_o}\right)_{e.p.} = .42 \left(\frac{m_b}{m}\right) \qquad \text{(Au)}$$

The umklapp processes account for 77% of the value for Ag, and 86% for Au.

We have set $n_o(E_F) = (3N/2E_F)(m_b/m)$, where m_b is the effective mass that would be obtained from a band structure calculation. The existing band structure calculations for Ag and Au are not in much agreement, and the published values for the band mass m_b (in units of m) vary between .88 and .98 for Ag; and between .85 and 1.01 for Au. See [38,39,40] and references therein.

If we use our calculated values for $(\Delta\gamma)_{ep}$ and work backwards, we find band masses of .79 and .81 for Ag and Au respectively. These values seem somewhat low, of course, but in view of the existing disparity in the literature, one should use Moriarty's pseudopotentials to calculate the band structure as well, if one is to make a sensible comparison. As one may see from Fig. 7, Moriarty's pseudopotentials are quite large, especially in the backward direction, and may well alter the band mass (relative to the free electron value) more than the potentials used in previous calculations.

§4.5 Interference Term for Ag-Au

Following the same procedure as before, we use (4.7), with ΔW obtained from Moriarty's pseudopotentials, to calculate the interference contribution for the

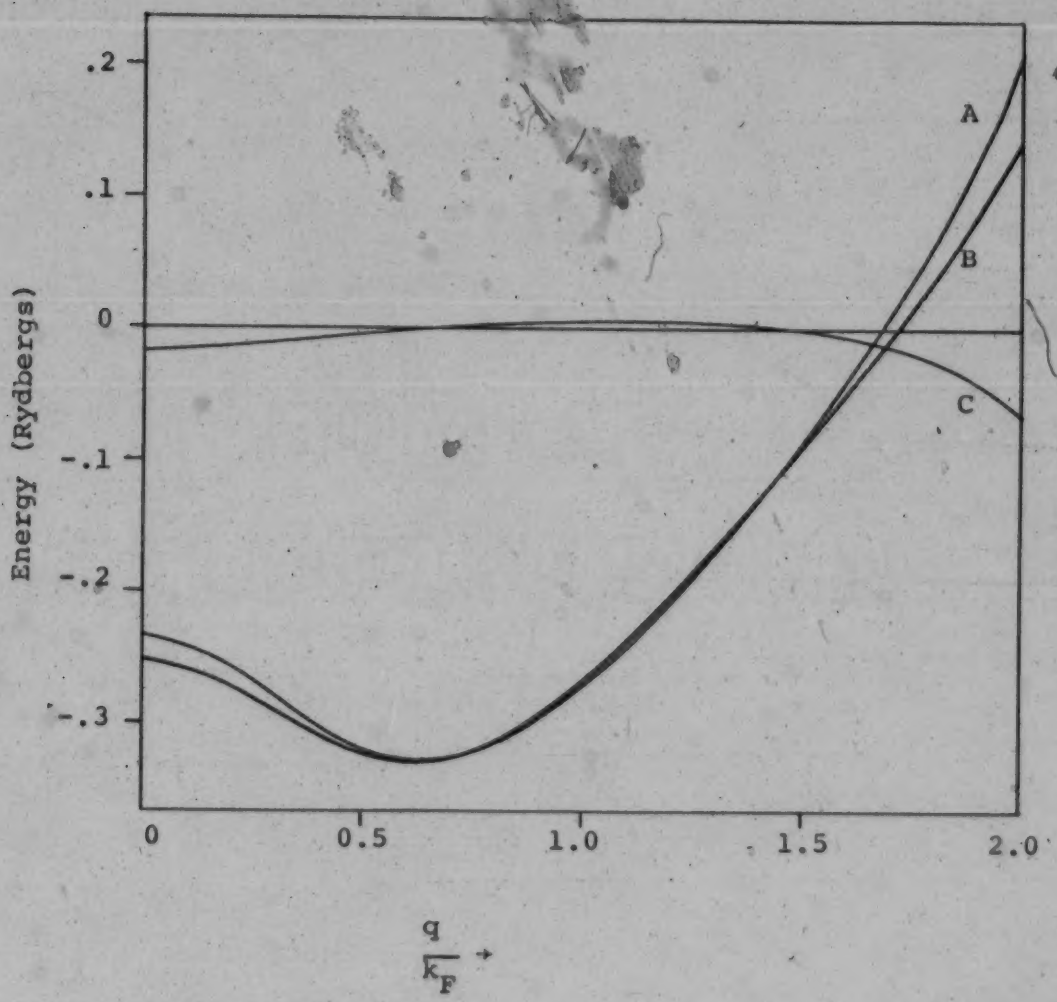

Fig. 7. Moriarty's pseudopotentials for the Ag-Au system. A - Au, B - Ag, C - (Ag-Au).

Ag-Au system. We take $E_F/Ms^2 = .29$, i.e. the simple average of the pure metal values, and thus arrive at

$$\left(\frac{\Delta\gamma}{\gamma_o}\right)_{int} = -.037\ c(1-c)\left(\frac{m_b}{m}\right)$$

with this value coming entirely from the umklapp processes. This result is considerably smaller than it should be, and the problem appears to be with the pseudopotential differences used in the calculation. Indeed, if we use the same values for ΔW to calculate the residual resistivity of this alloy, we obtain:

$$\rho_o = \frac{9\pi^3\hbar^2 c(1-c)}{e^2(2mE_F)^{\frac{1}{2}}E_F^2}\int_0^1 dx\, x^3 |\Delta W(x)|^2$$

$$= 9.65\ c(1-c)\ \mu\Omega\text{-cm}$$

in contrast with the experimental value

$$\rho_o = 35.06\ c(1-c)\ \mu\Omega\text{-cm}$$

obtained by Davis and Rayne. Thus it would seem that the values of ΔW are too small, in the umklapp region at least, by almost a factor of two. This does not mean that the pseudopotentials for the pure metals are off by this much, of course, but since both of these functions rise steeply in the umklapp region, any small errors in each one will be magnified in the difference.

In fact, if one were to simply move the Ag pseudopotential to the right by 0.1 k_F, the differences would increase by more than a factor of two in this region.

Thus if we increase the values of ΔW by $(35.06/9.65)^{\frac{1}{2}}$ in the calculation of $\Delta\gamma_{int}$, we arrive at

$$\left(\frac{\Delta\gamma}{\gamma_o}\right)_{int} = -.13\ c(1-c)\left(\frac{m_b}{m}\right)$$

which is a substantial contribution to the experimental value ($-.138\ c(1-c)$), even if the band mass is as low as .8.

§4.6 Impurity Term for Ag-Au

We cannot use ΔW from Moriarty's pseudopotentials to calculate $\Delta\gamma_{imp}$, since the values are not given for $q > 2k_F$. We may note, however, from Fig. 7, that ΔW is practically zero for $q < 1.5\ k_F$ and begins to increase, presumably to a peak just to the right of $2k_F$. At large values of q the pseudopotentials will be again essentially zero. Thus we may tentatively expect the "alloying potential" (ΔW) for Ag-Au to be peaked at one value of q and to decrease rather quickly away from this value.

There is some "circumstantial" evidence to support this view if we consider the Cd-Mg-Hg system. All

three of these elements have essentially the same valence, size, and Fermi energy, just as do Ag and Au. The data published by Inglesfield [41] on the alloys of these three metals demonstrates that the "alloying-wavenumber characteristic", which is essentially $|\Delta W|^2$ times the screening function appearing in (4.7), has a pronounced peak for a particular value of q, and falls off rapidly otherwise.

At any rate, to obtain some idea of what might be the case for Ag-Au, we take a simple functional form for $|\Delta W|^2$ and calculate f_{int} and f_{imp}. We choose:

$$|\Delta W(x)|^2 = A^2 x^2 \, e^{-(x/x_1)^2}$$

which has a single peak at $q = q_1 = 2k_F x_1$, and perform the computations for q_1 varying between 0 and 4 k_F, taking $E_F/Ms^2 = .29$. The principal value integration for f_{imp} is readily performed by noting that

$$\int_0^\infty dx \, \frac{e^{-\alpha^2 x^2}}{x^2-1} = -\sqrt{\pi}\, e^{-\alpha^2} \int_0^\infty e^{x^2} \, dx$$

which is easily evaluated numerically. The results are given in Fig. 8 as a function of q_1. We see the characteristic change of sign for f_{imp} as the weight of the integrand shifts to the right, while f_{int} becomes monotonically more negative.

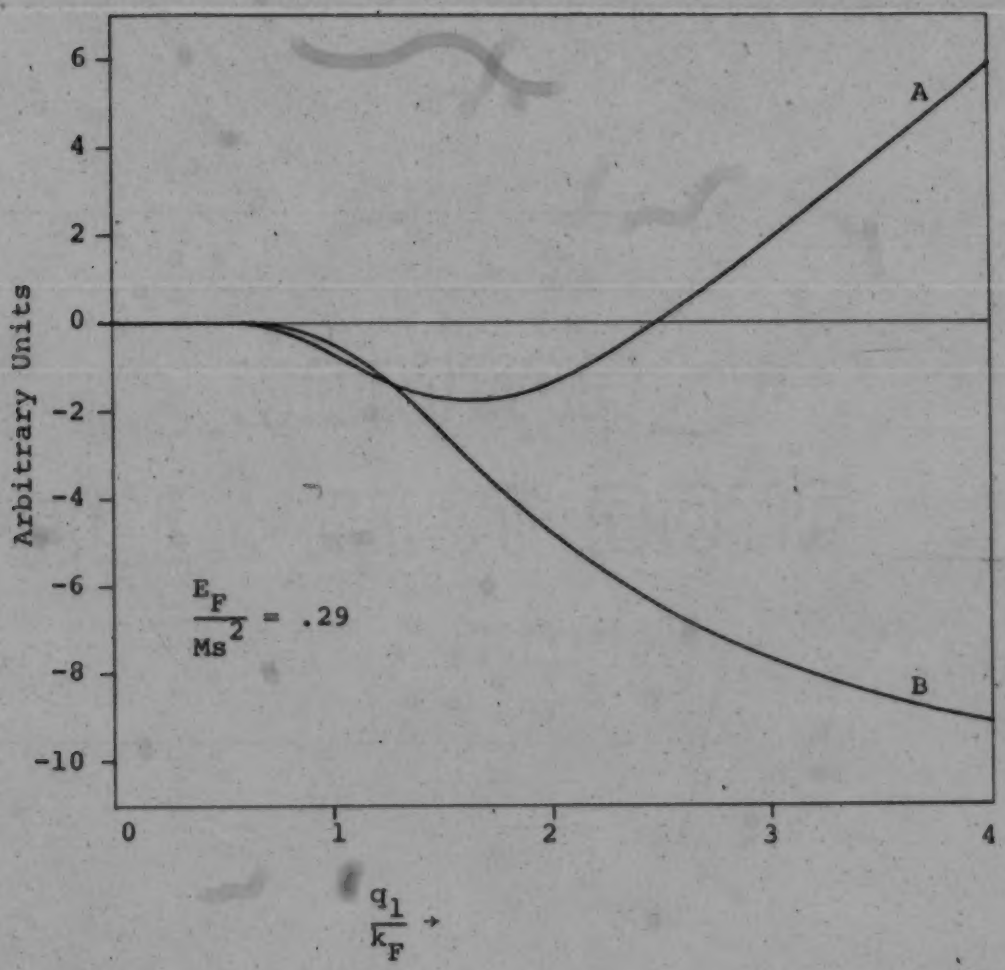

Fig. 8. Interference and impurity terms for the form of alloying potential considered in §4.6. A - f_{imp}, B - f_{int}.

A reasonable inference from this calculation is that the impurity term for Ag-Au alloys is small, and possibly of either sign, and that the interference term causes most of the deviation from linearity (in concentration) of the specific heat coefficient at $T = 0$.

At high temperatures, of course, only the static impurity term will survive, since the dynamic effects of the electron-ion interaction become negligible in this limit, as we have remarked earlier. This fact may, indeed, provide a means of experimentally determining the relative importance of these two contributions. The electron paramagnetic susceptibility, for instance, depends on the density of states, and can be measured both at high and low temperatures. At the present time, however, detailed data that would permit such a comparison do not seem to be available.

§4.7 Concluding Remarks on Interference and Impurity Contributions

From the results of the preceding sections, we may conclude that, in addition to the well-known importance of the electron-phonon enhancement, the dynamic "interference" effects are as important as, and actually tend to dominate the static "impurity" effects at low

temperatures. This is mainly due to the fact that the umklapp processes give rise to large peaks in the structure factor close to the reciprocal lattice vectors.

For monovalent metals, the shortest such vector is larger than $2k_F$, and thus only the steep "shoulder" of the structure factor enters the calculation. For the polyvalent metals, one or more of these peaks are included in the range of integration, and one may expect the dynamic effects to become even more pronounced.

CHAPTER 5

SUMMARY AND CONCLUSIONS

We have developed a formalism which describes, in second order perturbation theory, those thermodynamic properties of a metallic system arising from the electron-ion interaction. The central result is given by an expression for the free energy in terms of the electron-ion pseudopotentials and the dynamical structure factors of the ionic system.

This result may be applied to the wide range of metals (and their solid and liquid alloys) which may be adequately treated by pseudopotential methods. By using appropriate dynamical structure factors (whether theoretically or experimentally determined) the formalism allows for arbitrary dynamic properties of the ionic system, and is valid for alloys in which mass differences and lattice distortion (due to volume differences etc.) play an important role.

A significant aspect of the central formula is that it embodies, in a single concise expression, many results which are usually treated quite separately, using a variety of different techniques, which are often difficult to extend without a complete reformulation.

We have shown how one may simply obtain a number of such results from the general formalism, and have further derived a concise expression for the low-temperature electronic specific heat changes in a substitutional alloy, due to the dynamic part of the electron-ion interaction. In the numerical calculations we use this formula to perform some simple illustrative calculations of the electron-phonon enhancement factor.

An interesting part of the calculations was concerned with a comparison of the relative importance of the dynamic "interference" and static "impurity" contributions to the low-temperature electronic specific heat coefficient in binary alloys.

For a series of "theoretical" alloys, both of these terms were found to fall generally within the same order of magnitude, with the interference term demonstrating a tendency to dominate. The importance of this term is largely due to the fact that the umklapp processes give rise to pronounced peaks in the structure factors near reciprocal lattice vectors, an effect which is well known in resitivity calculations.

For Ag-Au alloys, the deviation from linearity (in concentration) of the low-temperature electronic

specific heat coefficient was examined, and our results seem to indicate that the interference term in this case is capable of adequately accounting for both the general magnitude and concentration dependence of the observed behaviour.

The relative importance of the interference and impurity terms might actually be determined experimentally from electron paramagnetic susceptibility measurements. This property is proportional to the density of states, and is measurable both at high and low temperatures. At high temperatures the interference term, along with the other dynamic parts of the electron-ion interaction, become negligible, while the static impurity term remains essentially unchanged. One might thus be able to separate the two terms in this way, if detailed experimental data were available.

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